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First Named Inventor	Yutaka Oka
Art Unit	1752
Examiner Name	Thorl Chea
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Remarks

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Application NO: 10/602,622  
Attorney Docket: FST-031381



DECLARATION

I, Machiko Shoji, a staff member of TAIYO, NAKAJIMA & KATO, 3-17, Shinjuku 4- chome, Shinjuku-ku, Tokyo 160-0022, Japan, do hereby declare that I am well acquainted with the English and Japanese languages and I hereby certify that, to the best of my knowledge and belief, the following is a true and correct translation made by me into the English language of the documents in respect of Japanese Patent Application No. 2002-232959, that was filed on 9th August 2002 in the name of FUJI PHOTO FILM CO., LTD.

Dated this 18th day of May, 2006

Machiko Shoji

Machiko Shoji

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[CONSIGNEE]	The Director General of the Patent Office	
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SPECIFICATION

[TITLE OF THE INVENTION]

## PHOTOTHERMOGRAPHIC MATERIAL

[CLAIMS]

[Claim 1] A photothermographic material comprising a support including on one surface thereof at least a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent for reducing silver ions and a binder, wherein the photosensitive silver halide 1) has a silver iodide content ranging from 10 mol% to 100 mol% and 2) contains two metals or more comprising at least one metal selected from the following first metal group and at least one metal selected from the following second metal group:

(First metal group)

iridium, ruthenium, iron, osmium and copper;

(Second metal group)

iridium, ruthenium, iron, osmium, rhenium, gold, platinum, copper, indium, gallium, lead, thallium, chromium, palladium, nickel and zinc,

with a proviso that none of the at least one metal selected from the first metal group and the at least one metal selected from the second metal group are the same.

[Claim 2] The photothermographic material according to claim 1,



wherein the photosensitive silver halide comprises a combination of metals selected from the first metal group and the second metal group such that the combinations to select from are (Ir-Fe), (Ir-Cu), (Ru-Cu), (Ru-Fe), (Fe-Os), (Fe-Ru), (Fe-Cu), (Fe-Pt), (Os-Cu), (Os-Fe), (Cu-Fe) and (Cu-Ru).

[Claim 3] The photothermographic material according to claim 1, wherein the photosensitive silver halide comprises a combination of metals selected from the first metal group and the second metal group such that the combinations to select from are (Ir-Fe), (Ru-Fe), (Fe-Cu), (Fe-Pt), (Ru-Cu), (Os-Fe), (Cu-Fe) and (Cu-Ru).

[Claim 4] The photothermographic material according to claim 1, wherein the metal selected from the first metal group is distributed in a core and the metal selected from the second metal group is distributed in a shell.

[Claim 5] The photothermographic material according to any one of claims 1 to 4, wherein an emulsion of the silver halide is chemically sensitized by at least one sensitization selected from the group consisting of chalcogen sensitization, gold sensitization and reduction sensitization.

[Claim 6] The photothermographic material according to claim 5, wherein the chalcogen sensitization is at least one of tellurium

sensitization, selenium sensitization and sulfur sensitization.

[Claim 7] The photothermographic material according to claim 5 or 6, wherein the chalcogen sensitization is at least one of tellurium sensitization and selenium sensitization.

[Claim 8] The photothermographic material according to any one of claims 5 to 7, wherein the chalcogen sensitization is tellurium sensitization.

[Claim 9] The photothermographic material according to any one of claims 1 to 8, wherein the silver iodide content of a photographic emulsion of the silver halide ranges from 40 mol% to 100 mol%.

[Claim 10] The photothermographic material according to claim 9, wherein the silver iodide content of the photographic emulsion of the silver halide ranges from 90 mol% to 100 mol%.

[Claim 11] The photothermographic material according to any one of claims 1 to 10, wherein a grain size of a grain of the silver halide ranges from 10 nm to 50 nm.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Industrial Field of the Invention]

The present invention relates to a photothermographic material. More particularly, the present invention relates to a photothermographic material that uses silver halide emulsion having a high silver iodide content, and that exhibits high sensitivity and low fog, and is excellent in lightfastness of images after receiving development treatment.

[0002]

[Prior Art]

In recent years in the medical field, it has been strongly desired to reduce the volume of processing waste fluids from the standpoints of environmental protection and conservation of space. Thus, there has been a need for technologies relating to photothermographic materials which are applicable for medical diagnosis or photographic technologies and can efficiently be exposed by a laser image setter or a laser imager to form clear black images having high resolution and sharpness. These photothermographic materials are advantageous in providing customers with a thermally developing system that does not need liquid-type processing solutions, and which is simple and not harmful to the environment. There is also a need for the similar technologies in the field of ordinary image forming materials. In particular in the field of medical diagnosis, which requires detail depiction, high quality images excellent in sharpness and graininess are needed and blue black image tone is desired in view of diagnosing

readiness. Currently, various types of hard copy systems using pigments and dyes, for example, ink jet printers and electrophotographic systems are widely used as the ordinary imaging system. However, the materials are not yet satisfactory in view of image quality (sharpness, graininess, gradation and tone) for providing diagnostic ability necessary for medical images and recording speed (sensitivity), and they have not yet reached a level at which they can replace existent medical films containing silver salts, that are used in a conventional wet developing system.

[0003]

On the other hand, photothermographic image forming systems using organic silver salts are described, for example, in U.S. Patent Nos. 3,152,904 and 3,457,075, and in "*Thermally Processed Silver Systems*" written by B. Shely, "*Imaging Processes and Materials*" written by Neblette, 8th Ed., edited by J. Sturge, V. Walworth & A. Shepp, p. 2, 1996. In particular, photothermographic materials generally have a photosensitive layer in which a photosensitive silver halide, a reducing agent, a reducible silver salt (e.g., organic silver salt), and optionally a toning agent for adjusting silver color tone are dispersed in a binder matrix.

[0004]

The photothermographic materials are, after having been imagewise exposed, heated to an elevated temperature (e.g., at 80°C or

higher) to form black silver images through a redox reaction between a reducible silver salt (serving as an oxidizing agent) and a reducing agent. The redox reaction is accelerated by catalytic action of latent images which have been formed on silver halides exposed to light. Therefore, the black silver images are formed in the exposed area. The photothermographic materials are disclosed in lots of patent documents such as U.S. Patent No.2,910,377 and Japanese Patent Application Publication (JP-B) No.43-4924. For a practical use, the Fuji Medical Dry Imager (FM-DP L) was marketed as a medical diagnostic image-forming system utilizing the photothermographic materials.

[0005]

Since such an image forming system utilizing the organic silver salt does not employ a fixing step, it is problematic in that after development treatment, image preservation is adversely affected, especially when the printed out image is exposed to light. In order to improve this printout problem, a method utilizing AgI formed by converting the organic silver salt is disclosed in U.S. Patent No. 6143488 and E.P. No. 0922995. However, these methods of utilizing the conversion of the organic silver salt with iodine were incapable of obtaining sufficient sensitivity, and were thus unable to create practically applicable systems. Other photosensitive materials utilizing AgI are disclosed in WO97/48014, WO97/48015, U.S. Patent No. 6165705, Japanese Patent Application Laid-Open (JP-A) No.

8-297345, and Japanese Patent No. 2785129, however, these could not achieve sufficient sensitivity or fogging levels, and hence, these materials are unsuitable for actual use as photosensitive materials exposed with lasers.

[0006]

Means for increasing sensitivity of a photographic silver iodide emulsion have been known by the photographic silver iodide emulsion being immersed in halogen receptors such as sodium nitrite, pyrogallol and hydroquinone or an aqueous silver nitrate solution, or by using sulfur sensitization at pAg 7.5 have been known, and the means are disclosed in publications such as the *Journal of Photographic Science*, Vol. 8, page 119 (1960), *ibid.* Vol. 28, page 163 (1980), or *Photographic Science and Engineering*, Vol. 5, page 216 (1961). However, as shown in Examples herein, the sensitizing effects exhibited by these halogen receptors were very poor and insufficient in the photothermographic material as disclosed herein.

[0007]

Doping a photosensitive silver halide with a heavy metal has been carried out on a variety of silver halides. For example, doping a transition metal belonging to Groups VI to X of the Periodic Table into the inside a silver halide grain is described in JP-A No. 2001-42471. It is preferable that a larger amount of the doping material is distributed on a surface of the grain or in the vicinity thereof rather

than inside the grain, or is uniformly distributed within the grain so as to exhibit high sensitivity. As such silver halides, silver bromide, silver iodobromide and silver chloriodobromide are used with a silver iodide content ranging from 0.01 mol% to 10 mol%, and preferably from 0.1 mol% to 5 mol%.

[0008]

On the other hand, JP-A No. 2000-66325 discloses a method for doping a silver halide grain with an iridium-type dopant and a transition metal dopant other than iridium, localized in mutually different regions, to obtain high sensitivity. In particular, the effect of the method to enhance sensitivity at the time when irradiated with high intensity light is set forth. As the silver halides, similar to the above, silver bromide, silver iodobromide, silver chloriodobromide and silver iodide are used with a silver iodide content ranging from 0.01 mol% to 10 mol%, and preferably from 0.1 mol% to 5 mol%. It is also described therein that such a doping method is applicable to a multi-color photosensitive material having two or more silver halide emulsion layers, however, there is no mention that this method is applicable to a photothermographic material.

[0009]

As described above, for use in the silver halide emulsions having a silver iodide content of 10 mol% or less, preferable heavy metals and preferable methods for adding such metals are

conventionally known, however, for use in the silver halide emulsions having a high silver iodide content of 40 mol% or more, no metals or methods are known whatsoever. The silver halide emulsion having such a high silver iodide content exhibits characteristics that differ completely from those of the silver halide emulsion having a silver iodide content of 10 mol% or less. When doping of a heavy metal ion is carried out, known technologies pertaining to the silver halide emulsion having a silver halide content of 10 mol% or less cannot be applied, and therefore, development of a new technology has become necessary.

Conventionally, silver halides having a high silver iodide content were not put into practical use, for the reasons detailed above. Accordingly, there has been no interest or motivation in doping of heavy metals, not to mention any interest in applying such doping to photothermographic materials.

[0010]

[Problems to be Solved by the Invention]

It is an object of the present invention is to provide a photothermographic material having a high silver iodide content that exhibits high sensitivity and low fog, and further is excellent in lightfastness of images.

[0011]

The above-described problems can be solved by the means



described below.

1) A photothermographic material comprising a support including on one surface thereof at least a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent for reducing silver ions and a binder, wherein the photosensitive silver halide 1) has a silver iodide content ranging from 10 mol% to 100 mol% and 2) contains two species or more comprising at least one metal selected from the following first metal group and at least one metal selected from the following second metal group:

(First metal group)

iridium, ruthenium, iron, osmium and copper;

(Second metal group)

iridium, ruthenium, iron, osmium, rhenium, gold, platinum, copper, indium, gallium, lead, thallium, chromium, palladium, nickel and zinc,

with a proviso that none of the at least one metal selected from the first metal group and the at least one metal selected from the second metal group are the same.

2) The photothermographic material according to 1), wherein the photosensitive silver halide comprises a combination of metals selected from the first metal group and the second metal group such that the combinations to select from are (Ir-Fe), (Ir-Cu), (Ru-Cu), (Ru-Fe), (Fe-Os), (Fe-Ru), (Fe-Cu), (Fe-Pt), (Os-Cu), (Os-Fe), (Cu-Fe) and (Cu-Ru).

3) The photothermographic material according to 1), wherein the

photosensitive silver halide comprises a combination of metals selected from the first metal group and the second metal group such that the combinations to select from are (Ir-Fe), (Ru-Fe), (Fe-Cu), (Fe-Pt), (Ru-Cu), (Os-Fe), (Cu-Fe) and (Cu-Ru).

4) The photothermographic material according to 1), wherein the metal selected from the first metal group is distributed in a core and the metal selected from the second metal group is distributed in a shell.

5) The photothermographic material according to any one of 1) to 4), wherein an emulsion of the silver halide is chemically sensitized by at least one sensitization selected from the group consisting of chalcogen sensitization, gold sensitization and reduction sensitization.

6) The photothermographic material according to 5), wherein the chalcogen sensitization is at least one of tellurium sensitization, selenium sensitization and sulfur sensitization.

7) The photothermographic material according to 5) and 6), wherein the chalcogen sensitization is at least one of tellurium sensitization and selenium sensitization.

8) The photothermographic material according to any one of 5) to 7), wherein the chalcogen sensitization is tellurium sensitization.

9) The photothermographic material according to any one of 1) to 8), wherein the silver iodide content of a photographic emulsion of the silver halide ranges from 40 mol% to 100 mol%.

10) The photothermographic material according to 9), wherein the silver iodide content of the photographic emulsion of the silver halide

ranges from 90 mol% to 100 mol%.

11) The photothermographic material according to any one of 1) to 10), wherein a grain size of a grain of the silver halide ranges from 10 nm to 50 nm.

[0012]

[Embodiments]

The present invention will now be described in more detail hereinafter.

#### 1. Photothermographic Material

A photothermographic material according to the invention comprises a support having disposed on at least one surface thereof an image-forming layer containing a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent and a binder. Further, the photothermographic material according to the invention may preferably have a surface protective layer on the image-forming layer, or a back layer or a back protective layer on an opposite surface thereof.

The layer construction and the components contained therein will be described in detail below.

[0013]

##### 1-1. Image-forming layer

##### 1-1-1. Photosensitive Silver Halide

##### 1) Halogen Composition

It is essential in the invention that a photosensitive silver halide has a silver iodide content of from 40 mol% to 100 mol%. The remaining silver halides are not particularly limited and may be selected from the group consisting of: silver chloride, silver bromide, and organic silver salts such as silver thiocyanate and silver phosphate, with silver bromide or silver chloride being particularly preferable. If the silver halide having such a high silver iodide content is used, a desirable photothermographic material may be devised in which lightfastness of images after subjected to a developing treatment is enhanced, in particular fogging due to irradiation with light is remarkably suppressed.

[0014]

Further, from a viewpoint of enhancing lightfastness of images after subjected to the development treatment, the silver iodide content is preferably in the range of from 80 mol% to 100 mol%, more preferably in the range of from 85 mol% to 100 mol%, and most preferably in the range of from 90 mol% to 100 mol%.

[0015]

Regarding the halogen composition in individual grains, the halogen may be uniformly distributed throughout the grain, or may be stepwise distributed, or may be continuously distributed. Further, a silver halide grain having a core/shell structure may preferably be used. The structure has preferably 2 to 5 layers, and more preferably

2 to 4 layers. Still further, a silver iodide high-core structure in which a silver iodide content in a core portion is high, as well as a silver iodide high-shell structure in which a silver iodide content in a shell portion is high may preferably be used. Furthermore, a technique to localize silver chloride or silver bromide on the surface of the grains in an epitaxial manner may be preferably employed.

[0016]

## 2) Grain Size

As far as the silver halide of high silver iodide content according to the invention is concerned, a grain size is particularly important. When a size of the silver halide is large, a coating amount of the silver halide to achieve a required maximum density is increased. The present inventors have found that, when a large amount of the silver halide having a high silver iodide content is coated, development is seriously suppressed to thereby decrease sensitivity and also density stability against a development period becomes deteriorated, as a result, a grain size larger than a certain magnitude cannot achieve a maximum density in a predetermined development period of time. On the other hand, the inventors have found that, if the addition amount is restricted, sufficient development can be obtained even using such a silver iodide.

[0017]

Thus, if the silver halide having a high silver iodide content is

used, it is necessary to specify the size of a silver halide grain to be substantially smaller as compared with that of the conventional silver bromide or silver iodobromide having a low iodide content, for the purpose of achieving a sufficient maximum optical density. A grain size of the silver halide is preferably in the range of from 5 nm to 100 nm, more preferably in the range of from 5 nm to 55 nm, and particularly preferably in the range of from 10 nm to 45 nm. The term "grain size" as used herein is intended to include an average diameter obtained by converting a projected area observed by an electron microscope into a circular image having a corresponding area.

[0018]

### 3) Coating Amount

A coating amount of the silver halide grain to be applied is, per mol of silver in a non-photosensitive organic silver salt to be described below, in the range of from 0.5 mol% to 15 mol%, preferably in the range of from 0.5 mol% to 12 mol%, more preferably in the range below 10 mol%, even more preferably in the range of from 1 mol% to 9 mol%, and particularly preferably in the range of from 1 mol% to 7 mol%. The addition amount is important and should be suitably selected in order to sufficiently inhibit suppressed development caused by the silver halide having a high silver iodide content.

[0019]

### 4) Grain-forming method

A method for forming a photosensitive silver halide is well known in the art; for example, methods as described in Research Disclosure No. 17029 (June, 1978) and U.S. Patent No. 3,700,458 may be employed. Specifically, a method in which firstly a photosensitive silver halide is prepared by adding a silver-supplying compound and a halogen-supplying compound to gelatin or another polymer solution and thereafter the thus prepared photosensitive silver halide is combined with an organic silver salt is preferably employed. Further, a method as described in paragraphs [0217] to [0224] of JP-A No. 11-119374, a method as described in JP-A No. 11-352627, or a method as described in Japanese Patent Application No. 2000-42336 is preferably used.

[0020]

#### 5) Grain Shape

Silver halide grains may have various shapes including, for example, cubic grains, octahedral grains, tetradecehedral grains, dodecahedral grains, tabular grains, spherical grains, rod-like grains, and potato-like grains. Examples of preferred shapes include a conjugated grain as described in R. L. Jenkins et al., the *Journal of Photographic Science*, Vol. 28 (1980) P.164 - Fig. 1. Further, a grain in a tabular form as shown in FIG. 1, *ibid.*, can preferably be used. Cubic silver halide grains are especially preferred for use in the present invention. Also preferred are roundish silver halide grains with their corners rounded. The surface index (Miller index) of the outer surface

of the photosensitive silver halide grains for use in the present invention is not specifically limited, but it is preferred that the proportion of {100} plane, which ensures higher spectral sensitization when it has adsorbed a color-sensitizing dye, in the outer surface is large. Preferably, the proportion of {100} plane is at least 50 %, more preferably at least 65 %, and even more preferably at least 80 %. The Miller index expressed by the proportion of {100} plane can be obtained according to the method described in *J. Imaging Sci.*, written by T. Tani, 29, 165 (1985), based on the adsorption dependency of {111} plane and {100} plane for sensitizing dyes.

[0021]

#### 6) Heavy Metal

The photosensitive silver halide according to the present invention comprises at least a first doping metal and a second doping metal.

[0022]

In the present invention, when the first doping metal and the second doping metal are simultaneously used, higher sensitivity is produced by a synergistic effect than they are each singly used. It is preferable that these metals are localized in different regions from each other inside the silver halide grain. For example, it is preferable that a larger portion of the first metal is present in a core of the grain, while a larger portion of the second metal is present in a shell thereof.



Alternatively, it is also preferable that the first metal is localized in the shell portion, while the second metal is localized in the core portion. Or it may be possible to localize the first metal in the shell portion, while uniformly distributing the second metal within the entire grain. By localizing the metals in mutually different regions inside the grain, sensitizing effects exerted by the respective metals may synergistically be exhibited.

[0023]

In order to dope the silver halide grain with at least one of these metals, a method in which when the silver halide grain is formed, a complex of such a heavy metal is mixed with a water-soluble halogen ion solution or an aqueous solution of silver nitrate such that the heavy metal is incorporated into a crystal is ordinarily employed. A method for localizing the metal inside the crystal is controlled by choosing the suitable point of mixing the metal at a stage of crystal growth of the silver halide grain. For example, when a larger amount of the metal is localized in the core portion than in other portions, the metal to be doped is added at an earlier stage of grain formation. On the other hand, when a larger amount of the metal is localized in the shell portion than in other portions, the metal is mixed at a later stage, or alternatively, a method in which after the grain formation is completed, the metal to be doped is first doped in other fine grains and then the resultant fine grains are mixed in the silver halide grains whereby a metal ion is transferred from such fine grains to the silver

halide grains may also be employed.

[0024]

#### 6-1) First Metal Group

The first metal is selected from the group consisting of: iridium, ruthenium, iron, osmium and copper, with iridium and iron being preferable, and iridium and copper being particularly preferable.

It is preferable that the metal is used in the form of a complex in which the metal serves as a central metal.

[0025]

For example, metal complexes whose center metal is iridium are trivalent or tetravalent iridium complexes. Examples of such iridium complexes include a hexachloroiridium (III) complex salt, a hexachloroiridium (IV) complex salt, a hexabromoiridium (III) complex salt, a hexabromoiridium (IV) complex salt, a hexaiodoiridium (III) complex salt, a hexaiodoiridium (IV) complex salt, an aquapentachloroiridium (III) complex salt, an aquapentachloroiridium (IV) complex salt, an aquapentabromoiridium (III) complex salt, an aquapentabromoiridium (IV) complex salt, an aquapentaiodoiridium (III) complex salt, an aquapentaiodoiridium (IV) complex salt, a diaquatetrachloroiridium (III) complex salt, a diaquatetrachloroiridium (IV) complex salt, a diaquatetrabromoiridium (III) complex salt, a diaquatetrabromoiridium (IV) complex salt, a diaquatetraiodoiridium (III) complex salt, a diaquatetraiodoiridium (IV) complex salt, a triaquatrachloroiridium (III) complex salt, a triaquatrachloroiridium (IV)

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 a hexacyanoiron (II) complex salt, a hexachloroosmium (II) complex salt,  
 a hexabromoosmium (II) complex salt, a hexaiodoosmium (II) complex

salt, an aquapentachloroosmium (II) complex salt, an aquapentabromoosmium (II) complex salt, an aquapentaiodoosmium (II) complex salt, a diaquatetrachloroosmium (II) complex salt, a diaquatetrabromoosmium (II) complex salt, a diaquatetraiodoosmium (II) complex salt, a triaquatribromoosmium (II) complex salt, a triaquatrachloroosmium (II) complex salt, a hexammineosmium (II) complex salt, a hexacyanoosmium (II) complex salt, copper (I) acetate, copper (II) acetate, copper (I) nitrate, copper (II) nitrate, a tetrachlorocopper (I) complex salt, a tetrachlorocopper (II) complex salt, a tetrabromocopper (I) complex salt, a tetrabromocopper (II) complex salt, a tetraiodocopper (I) complex salt, a tetraiodocopper (II) complex salt, a tetramminecopper (I) complex salt, a tetramminecopper (II) complex salt, a tetracyanocopper (I) complex salt, and a tetracyanocopper (II) complex salt.

[0026]

In the photothermographic material according to the present invention, an amount of the first metal to be added is, per mol of silver halide, preferably in the range of from  $1 \times 10^{-8}$  mol to  $1 \times 10^{-1}$  mol, and more preferably in the range of from  $1 \times 10^{-6}$  mol to  $1 \times 10^{-2}$  mol.

[0027]

In the photothermographic material according to the present invention, the first metal may be distributed in any portion within the entire silver halide grain. It may uniformly be distributed within the

grain or may locally be distributed in the core portion, the center shell portion, on the surface of the grain, the vicinity thereof (shell), or the like. However, when it is localized, it is preferably localized in the core portion.

[0028]

#### 6-2) Second Metal Group

The second metal is selected from the group consisting of: ruthenium, iron, osmium, rhenium, gold, platinum, copper, indium, gallium, lead, thallium, chromium, palladium, nickel and zinc. Among these, ruthenium, iron, rhenium, gold, platinum and copper are preferable, and ruthenium and iron are particularly preferable.

It is preferable that this metal is included in the form of a metal complex salt thereof in the same manner as for the first metal.

[0029]

This metal may uniformly be distributed within the entire silver halide grain or may locally be present in the core portion, a center shell portion, on the surface of the grain, in the vicinity thereof, or the like. When the metal is localized, it is preferably localized on the surface of the grain or the vicinity thereof (shell).

[0030]

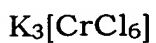
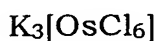
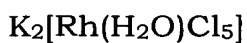
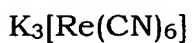
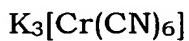
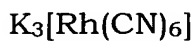
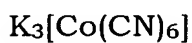
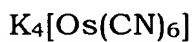
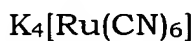
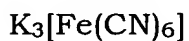
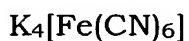
An amount of the second metal to be doped is, per mol of silver halide, preferably in the range of from  $1 \times 10^{-8}$  mol to  $1 \times 10^{-1}$  mol, more

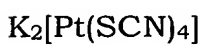
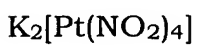
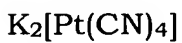
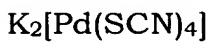
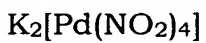
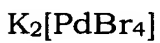
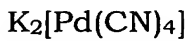
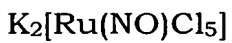
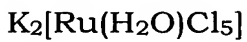
preferably in the range of from  $1 \times 10^{-6}$  mol to  $1 \times 10^{-2}$  mol, and still more preferably in the range of from  $1 \times 10^{-5}$  mol to  $5 \times 10^{-3}$  mol.

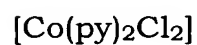
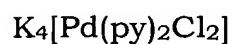
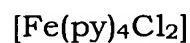
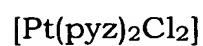
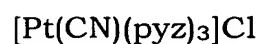
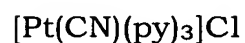
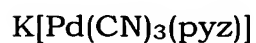
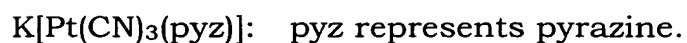
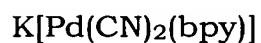
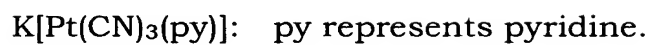
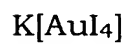
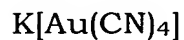
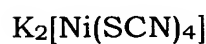
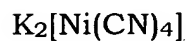
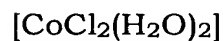
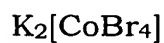
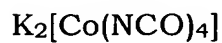
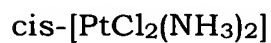
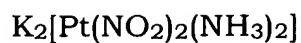
[0031]

Specific examples of metal complexes used in the present invention are given below. However, the present invention is not limited to these.

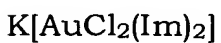
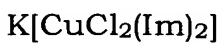
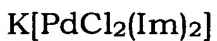
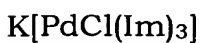
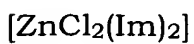
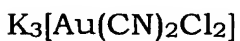
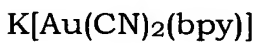
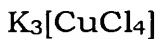
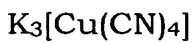
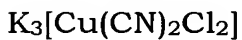
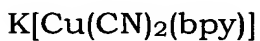
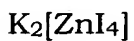
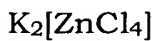
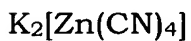
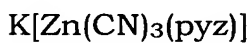
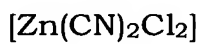
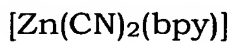
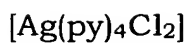
[0032]

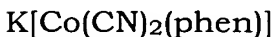
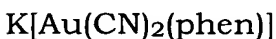
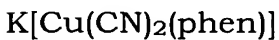
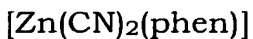
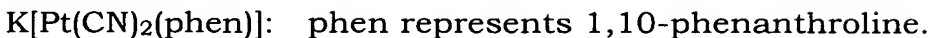
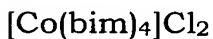
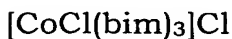
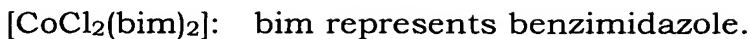
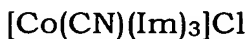
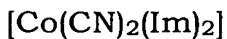
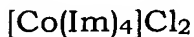
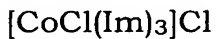
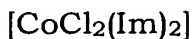
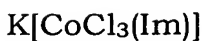












[0033]

### 6-3) Others

In the photothermographic material according to the invention, the photosensitive silver halide grain may contain, as a third metal different from the above-listed metals, a metal salt or a metal complex as described in JP-A No. 7-225449, paragraphs [0018] to [0024] of JP-A No. 11-65021, and paragraphs [0227] to [0240] of JP-A No. 11-119374.

[0034]

#### 6-4) Quantitative Determination of Doped Metal and Analysis of Distribution thereof within Grain

Quantitative determination of a doped metal and the distribution thereof within the photosensitive silver halide grain produced by the grain-forming method according to the invention may be confirmed through a method described in JP-A No. 2001-42471 and the like. Firstly, gelatin is separated by adding an aqueous actinase solution followed by centrifugal separation. Thereafter, a surface portion of the silver halide grain is gradually dissolved using an agent dissolving a silver halide such as an aqueous ammonia solution or an aqueous potassium cyanide solution, and then the concentration of the metal ion contained in the resultant supernatant is determined through a high frequency inductively coupled plasma mass spectrometry (ICP-MS), a high frequency inductively coupled plasma emission spectrometry (ICP-AES), or atomic absorption spectrometry.

[0035]

#### 7) Gelatin

Various types of gelatin may be used as gelatin to be contained in the photosensitive silver halide emulsion according to the invention. In order to maintain an excellent dispersion state of the photosensitive silver halide emulsion in a coating solution containing an organic silver salt, it is preferable to use a low molecular weight gelatin having a molecular weight in the range of from 500 to 60,000. These types of

gelatin may be used at the time of forming grains or at the time of dispersing operation after a desalting treatment is performed; however, they are preferably used at the time of dispersing operation after the desalting treatment is performed.

[0036]

#### 8) Chemical Sensitization

The photosensitive silver halide to be used in the invention may not be subjected to chemical sensitization; however, the photosensitive silver halide to be used in the invention is preferably chemically sensitized by at least one method selected from the group consisting of: chalcogen sensitization, gold sensitization and reduction sensitization. Examples of chalcogen sensitization include sulfur sensitization, selenium sensitization and tellurium sensitization.

[0037]

In the sulfur sensitization, an unstable sulfur compound is used and examples of the unstable sulfur compound include those as described, for example, in *Chimie et Physique Photographique*, 5th Ed., written by P. Grafkides, published by Paul Momtel (1987), and Research Disclosure, Vol. 307, No. 307105.

Specifically, at least one of conventionally known sulfur compounds such as thiosulfates (e.g., hypo), thioureas (e.g., diphenyl thiourea, triethyl thiourea, N-ethyl-N'-(4-methyl-2-thiazolyl)thiourea, and carboxymethyl trimethyl thiourea), thioamides (e.g.,

thioacetamide), rhodanines (e.g., diethyl rhodanine, 5-benzylidene-N-ethyl rhodanine), phosphine sulfides (e.g., trimethyl phosphine sulfides), thiohydantoins, 4-oxo-oxazolidine-2-thiones, disulfides or polysulfides (e.g., dimorpholine disulfide, cystine, and lenthionine), polythionates, elemental sulfur and the like, active gelatin and the like may be used. In particular, thiosulfates, thioureas and rhodanines are preferable.

[0038]

In the selenium sensitization, an unstable selenium compound is used. Examples of the usable selenium compound include those as described, for example, in JP-B Nos. 43-13489, and 44-15748, JP-A Nos. 4-25832, 4-109340, 4-271341, 5-40324, and 5-11385, Japanese Patent Application Nos. 4-202415, 4-330495, 4-333030, 5-4203, 5-4204, 5-106977, 5-236538, 5-241642, and 5-286916.

[0039]

Specifically, any one member selected from the group consisting of: colloidal metal selenium, selenoureas (e.g., N,N-dimethyl selenourea, trifluoromethylcarbonyl-trimethyl selenourea, and acetyl-trimethyl selenourea), selenamides (e.g., selenamide, and N,N-diethylphenyl selenamide), phosphine selenides (e.g., triphenyl phosphine selenide, and pentafluorophenyl-triphenyl phosphine selenide), selenophosphates (e.g., tri-p-tolylselenophosphate, and tri-n-butylselenophosphate), selenoketones (e.g., selenobenzophenone),

isoselenocyanates, selenocarboxylates, selenoesters, diacyl selenides and the like may be used. Further, at least one of non-unstable selenium compounds (e.g., selenious acid, selenocyanates, selenazoles and selenides) as described in JP-B No. 46-4553, 52-34492 and the like may be used, with phosphine selenides, selenoureas and selenocyanates being preferable.

[0040]

In the tellurium sensitization, an unstable tellurium compound is used. Examples of usable selenium compounds include those as described, for example, in JP-A Nos. 4-224595, 4-271341, 4-333043, 5-303157, 6-27573, 6-175258, 6-180478, 6-208186, 6-208184, 6-317867, 7-140579, 7-301879, and 7-301880.

[0041]

Specifically, any one member selected from the group consisting of: phosphine tellurides (e.g., butyl-diisopropyl phosphine telluride, tributyl phosphine telluride, tributoxy phosphine telluride, and ethoxy-diphenyl phosphine telluride), diacyl(di)tellurides (e.g., bis(diphenylcarbamoyl)ditelluride, bis(N-phenyl-N-methyl carbamoyl)ditelluride, bis(N-phenyl-N-methylcarbamoyl)telluride, bis(N-phenyl-N-benzylcarbamoyl)telluride, and bis(ethoxycarbonyl) telluride, telluroureas (e.g., N,N'-dimethylethylene tellurourea, and N,N'-diphenylethylene tellurourea), telluroamides, telluroesters, and the like may be used. In particular, diacyl(di)tellurides and phosphine

tellurides are preferable, and further, compounds as described in paragraph [0030] of JP-A No. 11-65021 and compounds represented by the general formulas (II), (III), and (IV) of JP-A No. 5-313284 are more preferable.

[0042]

Particularly, in the chalcogen sensitization employed in the invention, the selenium sensitization and the tellurium sensitization are preferable, with tellurium sensitization being particularly preferable.

[0043]

In the gold sensitization, at least one of gold sensitizers as described in *Chimie et Physique Photographique* written by P. Grafkides 5th Ed., published by Paul Momtel (1987), and Research Disclosure, Vol. 307, No. 307105 may be used. Specific examples of the gold sensitizer include chloroauric acid, potassium chloroaurate, potassium aurithiocyanate, gold sulfide and gold selenide, and gold compounds as described, for example, in U.S. Patent Nos. 2642361, 5049484, 5049485, 5169751, and 5252455, and Belgian Patent No. 691857. Further, at least one of the salts of other noble metals than gold such as platinum, palladium and iridium as described in *Chimie et Physique Photographique* written by P. Grafkides 5th Ed., published by Paul Momtel (1987), and Research Disclosure, Vol. 307, No. 307105 may also be used.

[0044]

The gold sensitization may be used either alone or in combination with the chalcogen sensitization. Specific examples thereof include gold-sulfur sensitization, gold-selenium sensitization, gold-tellurium sensitization, gold-sulfur-selenium sensitization, gold-sulfur-tellurium sensitization, gold-selenium-tellurium sensitization, and gold-sulfur-selenium-tellurium sensitization.

[0045]

According to the invention, the chemical sensitization may be performed at any time insofar as it is performed in any time from after the grain is formed to before the coating is performed, that is, the point of performing the chemical sensitization may be any time after desalting, at least one of (1) before the spectral sensitization, (2) simultaneously with the spectral sensitization, (3) after the spectral sensitization, (4) immediately before the coating, and the like.

[0046]

A use amount of the chalcogen sensitizer according to the invention is, varying depending on the silver halide grain to be used, chemical ripening conditions and the like, in the range of from  $10^{-8}$  mol to  $10^{-1}$  mol, and preferably in the range of approximately from  $10^{-7}$  mol to  $10^{-2}$  mol per mol of silver halide.

In the same manner as in the chalcogen sensitizer, a use



amount of the gold sensitizer according to the invention is, varying depending on various types of conditions, approximately in the range of from  $10^{-7}$  mol to  $10^{-2}$  mol, and preferably in the range of from  $10^{-6}$  mol to  $5 \times 10^{-3}$  mol per mol of silver halide. As to the atmosphere in which the emulsion is chemically sensitized, any condition may be selected; however, pAg is 8 or less, preferably 7.0 or less, more preferably 6.5 or less, and particularly preferably 6.0 or less; pAg is 1.5 or more, preferably 2.0 or more, and particularly preferably 2.5 or more; pH is in the range of from 3 to 10, and preferably in the range of from 4 to 9; and the temperature is in the range of from 20°C to 95°C, and preferably in the range of approximately from 25°C to 80°C.

[0047]

According to the present invention, reduction sensitization may be employed simultaneously with the chalcogen sensitization or the chemical sensitization. It is preferable that the reduction sensitization is employed simultaneously with the chalcogen sensitization.

Preferable examples of the compound usable in the reduction sensitization include ascorbic acid, thiourea dioxide, and dimethylamine borane, as well as stannous chloride, aminoiminomethane sulfinic acid, hydrazine derivatives, borane compounds, silane compounds, and polyamine compounds. Further, addition of a reduction sensitizer may be performed at any step in a manufacturing process of the photosensitive emulsion, that is, in a preparation process of from crystal growth to immediately before the

coating. Still further, the reduction sensitization is preferably performed by ripening the emulsion while maintaining the pH thereof at 8 or more, or the pAg thereof at 4 or less. Furthermore, the reduction sensitization is preferably performed by introducing a single addition portion of a silver ion during the grain formation.

A preferable amount of the reduction sensitizer to be added is, varying depending on various types of conditions in the same manner as in the chalcogen sensitizer or gold sensitizer, approximately in the range of from  $10^{-7}$  mol to  $10^{-1}$  mol, more preferably in the range of from  $10^{-6}$  mol to  $5 \times 10^{-2}$  mol per mol of silver halide.

[0048]

In the silver halide emulsion used in the invention, a thiosulfonic acid compound may be included through a method as described in EP-A No. 293,917.

It is preferable, from the standpoint of designing a high sensitive photothermographic material, that the silver halide grain according to the invention is chemically sensitized by at least one of the gold sensitization and the chalcogen sensitization.

[0049]

#### 9) Sensitizing Dye

As the sensitizing dye applicable to the invention, a sensitizing dye capable of spectrally sensitizing the silver halide grain in a desired wavelength region when adsorbed and having spectral sensitivity

appropriate to spectral characteristics of an exposure light source may advantageously be selected for use. It is preferable that the photothermographic material according to the invention is spectrally sensitized such that it has a spectral sensitive peak, particularly in the range of from 600 nm to 900 nm, or in the range of from 300 nm to 500 nm. The sensitizing dyes and addition methods thereof are described in paragraphs [0103] to [0109] of JP-A No. 11-65021, as compounds represented by the general formula (II) in JP-A No. 10-186572, as dyes represented by the general formula (I) in JP-A No. 11-119374, in paragraph [0106] of JP-A No. 11-119374, U.S. Patent No. 5,510,236, as dyes mentioned in Example 5 of U.S. Patent No. 3,871,887, in JP-A No. 2-96131, as dyes disclosed in JP-A No. 59-48753, in pp. 19 (line 38) to 20 (line 35) of EP-A No. 0803764, Japanese Patent Application Nos. 2000-86865, 2000-102560, and 2000-205399, and the like. The sensitizing dye may be used alone or in combination of two or more species thereof.

[0050]

An amount of the sensitizing dye according to the invention to be added is, desirably varying depending on sensitivity or fogging performance, preferably in the range of from  $1 \times 10^{-6}$  mol to 1 mol, and more preferably in the range of from  $1 \times 10^{-4}$  mol to  $1 \times 10^{-1}$  mol, per mol of silver halide in a photosensitive layer.

[0051]

According to the invention, in order to enhance spectral sensitizing efficiency, a super-sensitizer may be used. As to the super-sensitizers for use in the invention, mentioned are compounds described in, for example, EP-A No. 587,338, U.S. Patent Nos. 3,877,943 and 4,873,184, JP-A Nos. 5-341432, 11-109547 and 10-111543.

[0052]

#### 10) Simultaneous Use of Silver Halides

In the photothermographic material according to the invention, a single type of photosensitive silver halide emulsion may be used, or two or more types of silver halide emulsions (e.g., those having different average grain sizes, different halogen compositions, different crystal habits or different chemically sensitizing conditions from one another) may simultaneously be used. Use of plural types of photosensitive silver halides having different levels of sensitivity from one another makes it possible to control gradation. Relevant technologies are described, for example, in JP-A Nos. 57-119341, 53-106125, 47-3929, 48-55730, 46-5187, 50-73627 and 57-150841. Sensitivity difference among individual emulsions is preferably specified to be  $0.2\log E$  or more.

[0053]

#### 11) Mixing of Silver Halide and Organic Silver Salt

It is preferable that the photosensitive silver halide grain

according to the invention is formed at a position where a non-photosensitive organic silver salt is not present and then chemically sensitized. Such a procedure is employed because the method in which the silver halide is formed by adding a halogenating agent to the organic silver salt cannot attain sufficient sensitivity in some cases.

In order to mix the silver halide with the organic silver salt, employable are a method in which the photosensitive silver halide and the organic silver salt which have separately been prepared are mixed using a device selected from the group consisting of: a high-speed stirrer, a ball mill, a sand mill, a colloid mill, a vibration mill and a homogenizer, a method in which the photosensitive silver halide which has already been prepared is added at any desired point while the organic silver salt is being prepared to form a final organic silver salt, and the like. The advantageous effects of the invention may be suitably exerted by any of the above-described methods.

[0054]

#### 12) Mixing of Silver Halide to Coating Solution

A preferable point at which the silver halide according to the invention is added to a coating solution for an image-forming layer may be any time during a period of from 180 minutes before the coating is performed till immediately before the coating is performed, and preferably during a period of from 60 minutes before the coating is performed till 10 seconds before the coating is performed; however,

adding methods and conditions are not particularly limited, insofar as the advantageous effects of the invention can sufficiently be exerted. Specific mixing methods include, for example, a method of mixing ingredients in a tank such that an average dwelling time, as calculated from an adding flow rate and a supplying flow rate to a coater, is specified within a predetermined duration, and a method of using a static mixer or the like as described, for example, in N. Harnby, M. F. Edwards & A. W. Nienow, (translated by Koji Takahashi), "*Liquid Mixing Technology*" Chap. 8, published by the Nikkan Kogyo Shimbun, Ltd. (1989).

[0055]

#### 1-1-2. Explanation of Organic Silver Salt

A non-photosensitive organic silver salt in the invention is relatively stable to light, however, the silver salt forms silver images when heated to 80°C or more in the presence of an exposed photosensitive silver halide and a reducing agent. The organic silver salt may be any type of organic substances which contains sources which are able to reduce silver ions. Such non-photosensitive organic silver salts are described, for example, in paragraphs [0048] and [0049] of JP-A No. 10-62899, pp. 18 (line 24) to 19 (line 37) of EP-A No. 0803764, EP-A No. 0962812, JP-A Nos. 11-349591, 2000-7683, and 2000-72711. Silver salts of organic acids, particularly, long-chain aliphatic carboxylic acids (each having from 10 to 30 carbon atoms, preferably from 15 to 28 carbon atoms) are preferable. Preferable

examples of the organic silver salts include silver behenate, silver arachidate, silver stearate, silver oleate, silver laurate, silver caproate, silver myristate, silver palmitate, silver erucate and the mixture thereof. In the invention, use of the organic silver salt whose silver behenate content is 50 mol% to 100 mol% is preferable. It is particularly preferable that the silver behenate content in the organic silver salt is 75 mol% to 98 mol%.

[0056]

The shape of particles of an organic silver salt which can be used in the present invention is not particularly limited, and may be a needle, rod, plate or flake shape.

Preferably, a flaky organic silver salt is used in the present invention. Herein, flaky organic silver salts are defined as follows. If the salt is examined through an electron microscope and the shape of the particles is considered to be approximately a rectangular parallelepiped, its sides are named "a", "b" and "c" in an order beginning with the shortest dimension ("c" may be equal to "b"), and the values of the two shortest sides "a" and "b" are used to calculate "x" by the following equation:

$$x = b/a$$

[0057]

The value "x" is calculated for about 200 particles and if their mean value,  $x(\text{mean}) \geq 1.5$ , the particles are defined as flaky.

Preferably,  $30 \geq x(\text{mean}) \geq 1.5$ , and more preferably  $20 \geq x(\text{mean}) \geq 2.0$ . Incidentally, the particles are needle-shaped if  $1 \leq x(\text{mean}) < 1.5$ .

[0058]

Side "a" of a flaky particle can be regarded as the thickness of a plate-shaped particle having a principal face defined by sides "b" and "c". The mean value of "a" is preferably from 0.01 to 0.23  $\mu\text{m}$ , and more preferably from 0.1 to 0.20  $\mu\text{m}$ . The mean value of c/b is preferably from 1 to 6, more preferably from 1.05 to 4, still more preferably from 1.1 to 3, and particularly preferably from 1.1 to 2.

[0059]

The particle sizes of the organic silver salt preferably have a monodispersed size distribution. In the monodispersed distribution, the standard deviation of the length of the minor axis or major axis of the particles divided by a length value of the minor axis or major axis, respectively, is preferably not more than 100%, more preferably not more than 80%, and still more preferably not more than 50%. The shape of particles of the salt can be determined from an observed image of a dispersion thereof through a transmission electron microscope. The particle size distribution of the salt can alternatively be determined by employing the standard deviation of the volume weighted mean diameter of the particles, and is monodispersed if a percentage obtained by dividing the standard deviation of the volume



weighted mean diameter by the volume weighted mean diameter (coefficient of variation) is not more than 100%, more preferably not more than 80%, and still more preferably not more than 50%. The particle size (volume weighted mean diameter) can be determined, for example, by applying laser light to the organic silver salt dispersed in a liquid and determining an autocorrelation function of the variation of fluctuation of scattered light with time.

[0060]

Known methods can be employed to prepare and disperse an organic silver salt usable in the present invention. Reference may be made to, for example, Japanese Patent Application Laid-Open No. 10-62899, European Patent Laid-Open No. 0803763A1 and European Patent Laid-Open No. 962812A1, JP-A Nos. 11-349591, 2000-7683, and 2000-72711, Japanese Patent Application Nos. 11-348228 to 11-348230, 11-203413, 2000-90093, 2000-195621, 2000-191226, 2000-213813, 2000-214155, and 2000-191226.

[0061]

According to the present invention, the photosensitive material can be prepared by mixing an aqueous dispersion of an organic silver salt with an aqueous dispersion of a photosensitive silver salt. It is preferable, for controlling photographic properties, to mix two or more kinds of aqueous dispersions of organic silver salts with two or more kinds of aqueous dispersions of photosensitive silver salts.

[0062]

In the present invention, a desired amount of the organic silver salt may be used, but the amount of silver is preferably 0.1 to 5 g/m<sup>2</sup>, more preferably 1 to 3 g/m<sup>2</sup>, and particularly preferably 1.2 to 2.5 g/m<sup>2</sup>.

[0063]

#### 1-1-3. Reducing Agent

It is preferable that the photothermographic material according to the invention comprises a thermally developing agent which is a reducing agent for the organic silver salt. The reducing agent for the organic silver salt may be any substance (preferably an organic substance), so long as it can reduce a silver ion to metallic silver. Examples of such reducing agents include those as described in paragraphs [0043] to [0045] of JP-A No. 11-65021, and in pp. 7 (line 34) to 18 (line 12) of EP-A No. 0803764.

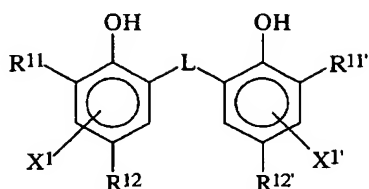
[0064]

Preferable reducing agents for use in the invention are so-called hindered phenol-type reducing agents having a substituent at an ortho position of a phenolic hydroxyl group, or bisphenol-type reducing agents. Particularly preferable are the compounds represented by the general formula (R) shown below. These compounds will now be described in detail.

[0065]

[F1]

General Formula (R)



[0066]

wherein  $R^{11}$  and  $R^{11'}$  each independently represent an alkyl group having from 1 to 20 carbon atoms;  $R^{12}$  and  $R^{12'}$  each independently represent a hydrogen atom or a substituent for the benzene ring; L represents a group of  $-S-$  or  $-CHR^{13}-$  in which  $R^{13}$  represents a hydrogen atom or an alkyl group having from 1 to 20 carbon atoms; and  $X^1$  and  $X^{1'}$  each independently represent a hydrogen atom or a substituent for the benzene ring.

[0067]

Now, each substituent will be described in detail.

1)  $R^{11}$  and  $R^{11'}$

$R^{11}$  and  $R^{11'}$  each independently represent an optionally substituted alkyl group having from 1 to 20 carbon atoms and the substituent for the alkyl group is not particularly limited. Preferable examples of such substituents include an aryl group, a hydroxyl group,

an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an acylamino group, a sulfonamide group, a sulfonyl group, a phosphoryl group, an acyl group, a carbamoyl group, an ester group, and a halogen atom.

[0068]

2)  $R^{12}$  and  $R^{12'}$ , and  $X^1$  and  $X^{1'}$

$R^{12}$  and  $R^{12'}$  each independently represent a hydrogen atom or a substituent for the benzene ring.

$X^1$  and  $X^{1'}$  each independently represent a hydrogen atom or a substituent for the benzene ring.

Preferable examples of the substituent for the benzene ring include an alkyl group, an aryl group, a halogen atom, an alkoxy group and an acylamino group.

[0069]

3) L

L represents a group -S- or a group -CHR<sup>13</sup>-, wherein  $R^{13}$  represents a hydrogen atom or an alkyl group having from 1 to 20 carbon atoms and the alkyl group may have a substituent.

Specific examples of the alkyl group as non-substituted  $R^{13}$  include a methyl group, an ethyl group, a propyl group, a butyl group, a heptyl group, an undecyl group, an isopropyl group, a 1-ethylpentyl group and a 2,4,4-trimethylpentyl group.

[0070]

Examples of substituents for the alkyl group, in the same manner as those for  $R^{11}$ , include a halogen atom, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an acylamino group, a sulfonamide group, a sulfonyl group, a phosphoryl group, an oxycarbonyl group, a carbamoyl group and a sulfamoyl group.

[0071]

#### 4) Preferable Substituents

$R^{11}$  and  $R^{11'}$  are preferably a secondary or tertiary alkyl group having from 3 to 15 carbon atoms. Specific examples of such alkyl groups include an isopropyl group, an isobutyl group, a t-butyl group, a t-amyl group, a t-octyl group, a cyclohexyl group, a cyclopentyl group, a 1-methylcyclohexyl group, and a 1-methylcyclopropyl group.  $R^{11}$  and  $R^{11'}$  are more preferably a tertiary alkyl group having from 4 to 12 carbon atoms, still more preferably a t-butyl group, a t-amyl group, and a 1-methylcyclohexyl group, and most preferably a t-butyl group.

[0072]

Preferably,  $R^{12}$  and  $R^{12'}$  are each independently an alkyl group having from 1 to 20 carbon atoms. Specific examples of such alkyl groups include a methyl group, an ethyl group, a propyl group, a butyl group, an isopropyl group, a t-butyl group, a t-amyl group, a cyclohexyl group, a 1-methylcyclohexyl group, a benzyl group, a methoxymethyl group, and a methoxyethyl group, and more preferably

a methyl group, an ethyl group, a propyl group, an isopropyl group and a t-butyl group.

[0073]

Preferably,  $X^1$  and  $X^{1'}$  are each independently a hydrogen atom, a halogen atom, and an alkyl group, and more preferably a hydrogen atom.

[0074]

L is preferably a group  $-\text{CHR}^{13}-$ .

[0075]

$R^{13}$  is preferably a hydrogen atom or an alkyl group having from 1 to 15 carbon atoms. Preferable examples of such alkyl groups include a methyl group, an ethyl group, a propyl group, an isopropyl group and 2,4,4-trimethylpentyl group. Particularly preferable examples of the alkyl group as  $R^{13}$  include a hydrogen atom, a methyl group, a propyl group and an isopropyl group.

[0076]

When  $R^{13}$  is a hydrogen atom,  $R^{12}$  and  $R^{12'}$  are each independently preferably an alkyl group having from 2 to 5 carbon atoms, with an ethyl group and a propyl group being more preferable and an ethyl group being most preferable.

[0077]

When  $R^{13}$  is a primary or secondary alkyl group having from 1 to 8 carbon atoms,  $R^{12}$  and  $R^{12'}$  are each independently preferably a methyl group. As the primary or secondary alkyl group having from 1 to 8 carbon atoms of  $R^{13}$ , a methyl group, an ethyl group, a propyl group and an isopropyl group are more preferable, with a methyl group, an ethyl group and a propyl group being still more preferable.

[0078]

When  $R^{11}$ ,  $R^{11'}$ ,  $R^{12}$ , and  $R^{12'}$  are each independently a methyl group,  $R^{13}$  is preferably a secondary alkyl group. In this case, as the secondary alkyl group of  $R^{13}$ , an isopropyl group, an isobutyl group, and a 1-ethylpentyl group are preferable and an isopropyl group is more preferable.

[0079]

The above-described reducing agents exert different thermal developing properties by the combination of  $R^{11}$ ,  $R^{11'}$ ,  $R^{12}$ ,  $R^{12'}$  and  $R^{13}$  suitably selected. Since the thermal developing properties may be controlled by simultaneously using at least two types of reducing agents at various mixing ratios, it is preferable, depending on applications, to use at least two types of reducing agents in combination.

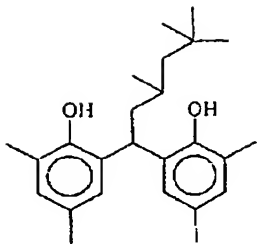
[0080]

Specific examples of the compound represented by the general formula (R) usable in the invention are shown below; however, the invention is not limited thereto.

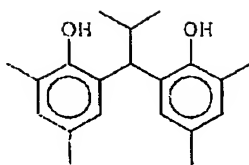
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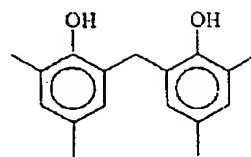
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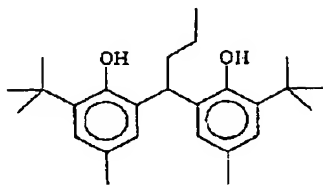
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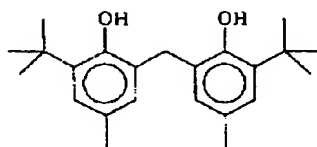
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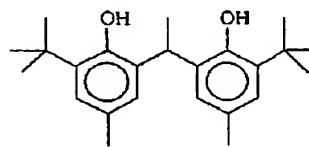
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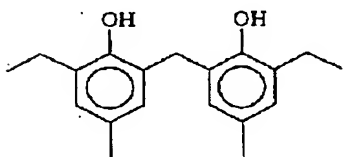
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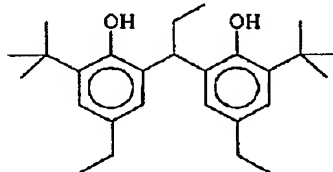
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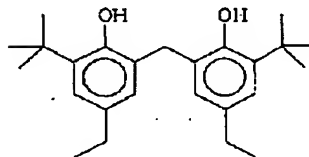
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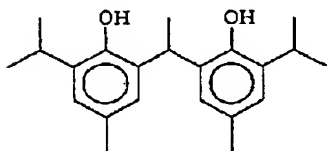
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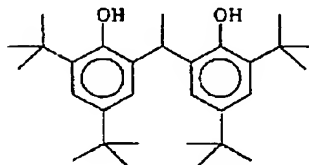
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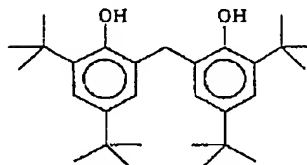
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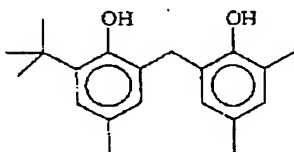
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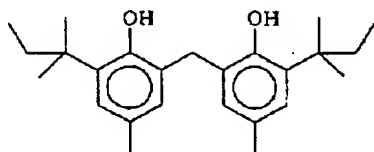
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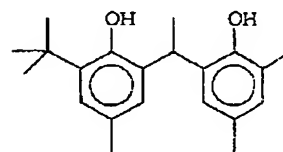
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(R-14)



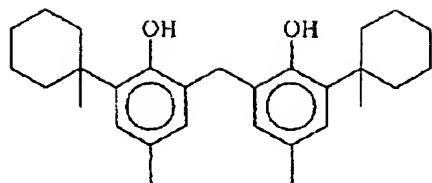
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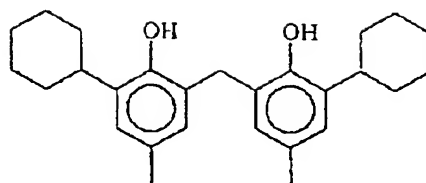
[0082]

[F3]

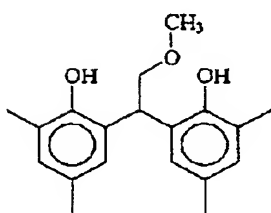
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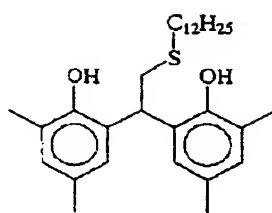
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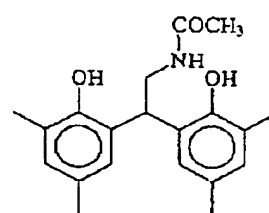
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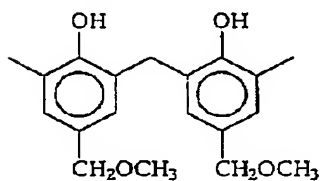
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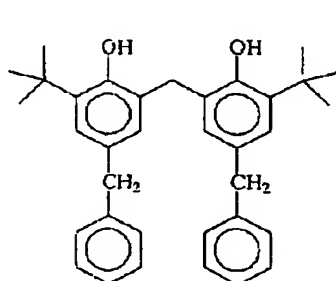
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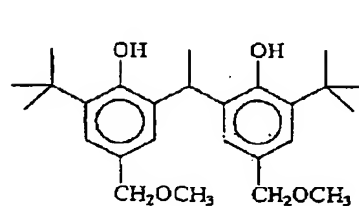
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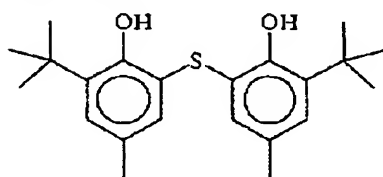
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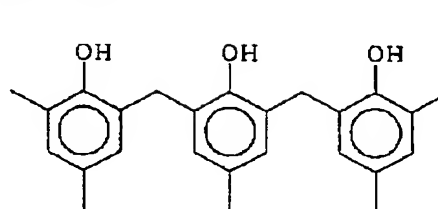
(R-23)



(R-24)



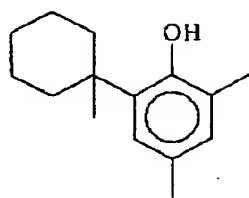
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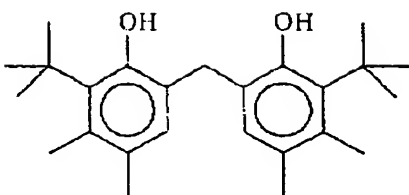
[0083]

[F4]

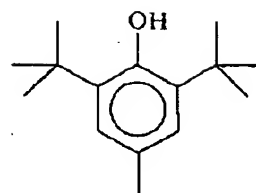
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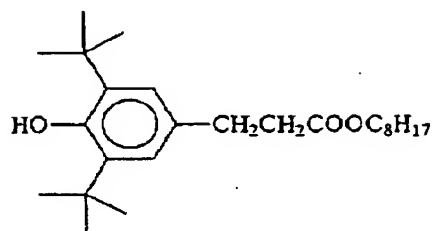
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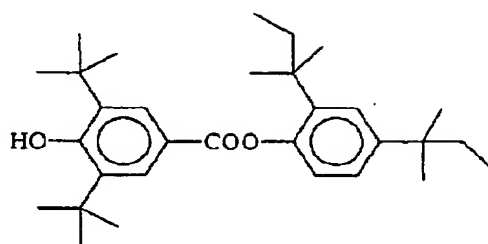
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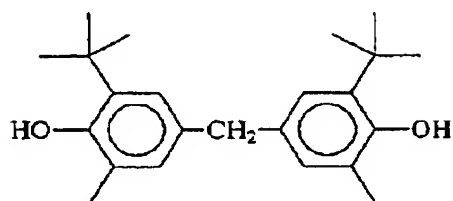
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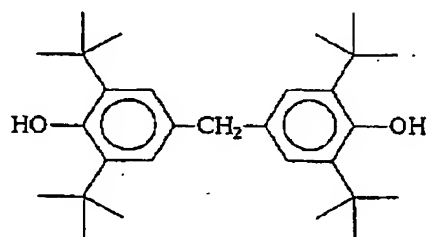
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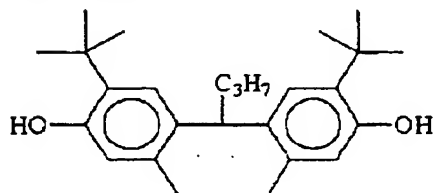
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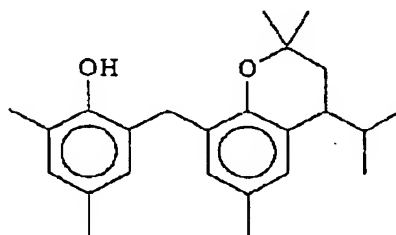
(R-32)



(R-33)



(R-34)



[0084]

Use of the compounds shown in (R-1) to (R-20) is particularly preferable.

[0085]

An amount of the reducing agent to be added in the invention is preferably in the range of from 0.01 g/m<sup>2</sup> to 5.0 g/m<sup>2</sup>, more preferably in the range of from 0.1 g/m<sup>2</sup> to 3.0 g/m<sup>2</sup>, per mol of silver on a surface provided with an image-forming layer, preferably in the range of from 5 mol% to 50 mol% and more preferably in the range of from 10 mol% to 40 mol%.

[0086]

Although the reducing agent according to the invention may be included in the image-forming layer containing the organic silver salt and the photosensitive silver halide, and a layer adjacent thereto, it is more preferable to include the reducing agent in the image-forming layer.

[0087]

In the invention, the reducing agent may be present in the coating solution in any form of a solution, an emulsified-dispersion, a solid fine particle dispersion and the like, and the resultant coating solution may be included in the photosensitive material.

[0088]

As the conventionally known emulsify-dispersing method, a method in which the reducing agent is dissolved using an oil such as dibutyl phthalate, tricresyl phosphate, glyceryl triacetate and diethyl phthalate, or an auxiliary solvent such as ethyl acetate and cyclohexanone, and thereafter the resultant solution is subjected to mechanical treatment to prepare an emulsified dispersion.

[0089]

Further, as solid fine particle dispersing methods, employable is a method in which the reducing agent is dispersed in an appropriate solvent such as water using a ball mill, a colloid mill, a vibration mill, a sand mill, a jet mill, a roller mill or an ultrasonic wave to prepare a solid dispersion. Preferably, the dispersing method is employed using the sand mill. Incidentally, any one of a protective colloid (e.g., polyvinyl alcohol), and a surfactant (e.g., an anionic surfactant such as sodium triisopropyl naphthalene sulfonate that is a mixture of different types of such sulfonates in which substitution positions of three isopropyl groups are different from one another) may be used. The aqueous dispersion may contain a preservative (e.g., sodium benzoisothiazolate).

[0090]

A particularly preferable method is the solid fine particle dispersing method. The reducing agent is added as fine particles

having an average particle size in the range of from 0.01  $\mu\text{m}$  to 10  $\mu\text{m}$ , preferably in the range of from 0.05  $\mu\text{m}$  to 5  $\mu\text{m}$ , and more preferably in the range of from 0.1  $\mu\text{m}$  to 1  $\mu\text{m}$ . According to the invention, it is preferable that any other solid dispersion is used employing the above-described ranges of particle sizes.

[0091]

#### 1-1-4. Developing Accelerator

In the photothermographic material according to the invention, sulfonamide phenolic compounds represented by the general formula (A) as described in JP-A Nos. 2000-267222 and 2000-330234, hindered phenolic compounds represented by the general formula (II) as described in JP-A No. 2001-92075, hydrazine-type compounds represented by the general formula (1) as described in Japanese Patent Application No. 2001-074278, and phenolic or naphtholic compounds represented by the general formula (2) as described in Japanese Patent Application No. 2000-76240 are preferably used. These developing accelerators are used, relative to the reducing agent, in the range of from 0.1 mol% to 20 mol%, preferably in the range of from 0.5 mol% to 10 mol%, and more preferably in the range of from 1 mol% to 5 mol%. The method of introducing the developing accelerator to the photosensitive material may be performed in the same manner as in the reducing agent, and particularly it is preferably incorporated after being changed into a solid dispersion or an emulsified dispersion. When the developing accelerator is incorporated in the form of the

emulsified dispersion, it is preferably incorporated in the form an emulsified dispersion prepared by dispersing operation using a high boiling solvent which is solid at room temperature and a low boiling auxiliary solvent, or in the form of a so-called oilless emulsified dispersion using no high boiling solvent.

[0092]

Among the above-described developing accelerators according to the invention, the hydrazine-type compounds represented by the general formula (1) as described in Japanese Patent Application No. 2001-074278 and the phenolic or naphtholic compounds represented by the general formula (2) as described in Japanese Patent Application No. 2000-76240 are particularly preferable.

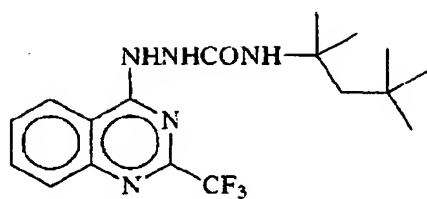
[0093]

Specific examples of developing accelerators according to the invention are described below; however, the invention is not limited thereto.

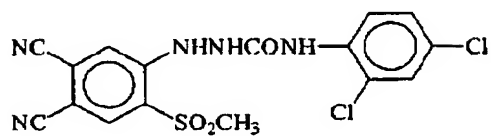
[0094]

[F5]

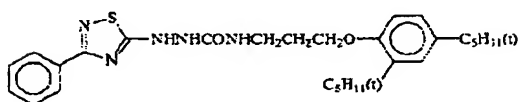
(A-1)



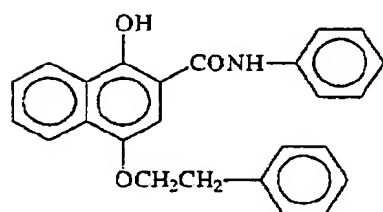
(A-3)



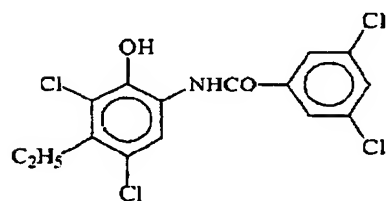
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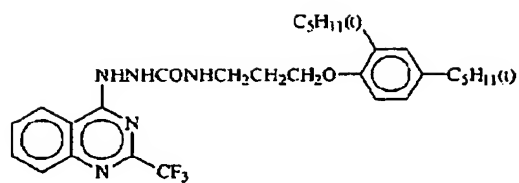
(A-7)



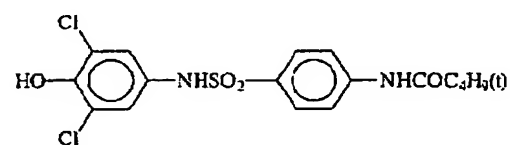
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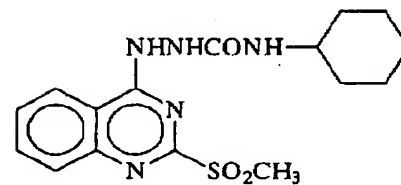
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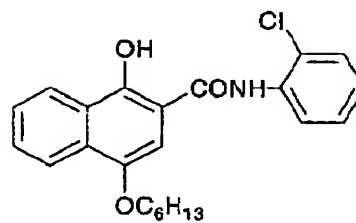
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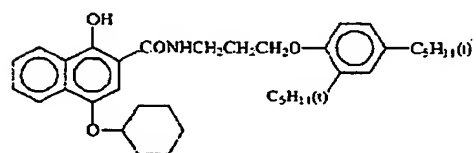
(A-6)



(A-8)



(A-10)



[0095]



#### 1-1-5. Hydrogen bond-forming compound

According to the invention, it is preferable that a non-reducing compound having a group capable of forming a hydrogen bond with a compound having an aliphatic hydroxyl group (-OH) of a reducing agent is simultaneously used.

[0096]

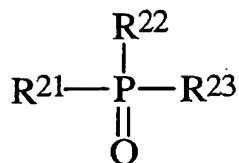
Examples of such groups capable of forming a hydrogen bond include a phosphoryl group, a sulfoxide group, a sulfonyl group, a carbonyl group, an amide group, an ester group, an urethane group, an ureido group, a tertiary amino group, and a nitrogen-containing aromatic group. Among these, compounds having a phosphoryl group, a sulfoxide group, an amide group (not having >N-H group but blocked like >N-Ra, in which Ra represents a substituent exclusive of H), an urethane group (not having >N-H group but blocked like >N-Ra, in which Ra represents a substituent exclusive of H), an ureido group (not having >N-H group but blocked like >N-Ra, in which Ra represents a substituent exclusive of H) are preferable.

[0097]

Particularly preferable hydrogen bond-forming compounds for use in the invention are compounds represented by the following general formula (D):

[0098]

[F6]



General Formula (D)

[0099]

wherein  $\text{R}^{21}$  to  $\text{R}^{23}$  each independently represent at least one group selected from the group consisting of: an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an amino group, and a heterocyclic group, which may be unsubstituted or substituted.

[0100]

When any one of  $\text{R}^{21}$ ,  $\text{R}^{22}$ , and  $\text{R}^{23}$  has a substituent, examples of such substituents include a halogen atom, an alkyl group, an aryl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an alkylthio group, an arylthio group, a sulfonamide group, an acyloxy group, an oxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group and a phosphoryl group; on this occasion the substituent is preferably an alkyl group or an aryl group, and examples of such alkyl groups and aryl groups include a methyl group, an ethyl group, an isopropyl group, a t-butyl group, a t-octyl group, a phenyl group, a 4-alkoxyphenyl group and a 4-acyloxyphenyl group.

[0101]

Specific examples of such alkyl groups of  $R^{21}$ ,  $R^{22}$ , and  $R^{23}$  include a methyl group, an ethyl group, a butyl group, an octyl group, a dodecyl group, an isopropyl group, a t-butyl group, a t-amyl group, a t-octyl group, a cyclohexyl group, 1-methylcyclohexyl group, a benzyl group, a phenethyl group and a 2-phenoxypropyl group.

[0102]

Specific examples of such aryl groups include a phenyl group, a cresyl group, a xylyl group, a naphthyl group, a 4-t-butylphenyl group, a 4-t-octylphenyl group, a 4-anisidyl group and a 3,5-dichlorophenyl group.

[0103]

Specific examples of such alkoxy groups include a methoxy group, an ethoxy group, a butoxy group, an octyloxy group, a 2-ethylhexyloxy group, a 3,5,5-trimethylhexyloxy group, a dodecyloxy group, a cyclohexyloxy group, a 4-methylcyclohexyloxy group and a benzyloxy group.

[0104]

Specific examples of such aryloxy groups include a phenoxy group, a cresyloxy group, an isopropylphenoxy group, a 4-t-butylphenoxy group, a naphthoxy group and a biphenyloxy group.

[0105]

Specific examples of such amino groups include a dimethylamino group, a diethylamino group, a dibutylamino group, a dioctylamino group, an N-methyl-N-hexylamino group, a dicyclohexylamino group, a diphenylamino group and an N-methyl-N-phenylamino group.

[0106]

As  $R^{21}$  to  $R^{23}$ , an alkyl group, an aryl group, an alkoxy group, or aryloxy group is preferable. From the standpoint of the effects exerted by the invention, it is preferable that at least one of  $R^{21}$  to  $R^{23}$  is an alkyl group or an aryl group, and it is more preferable that at least two of  $R^{21}$ ,  $R^{22}$  and  $R^{23}$  are an alkyl group or an aryl group. Further, taking availability at a low cost into consideration, it is preferable that  $R^{21}$  to  $R^{23}$  are the same groups.

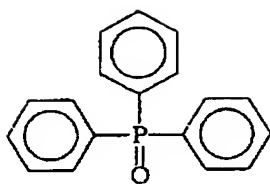
[0107]

Specific examples of hydrogen bond-forming compounds including the compound represented by the general formula (D) according to the invention are listed below; however, the invention is by no means limited thereto.

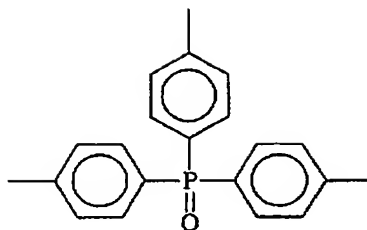
[0108]

[F7]

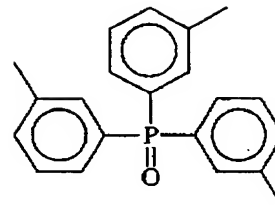
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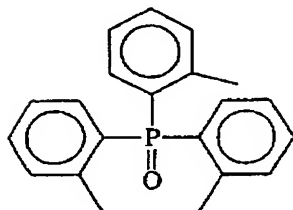
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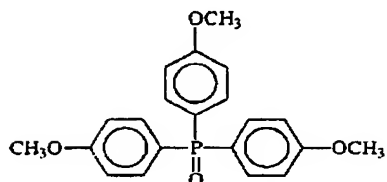
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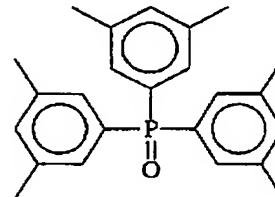
(D-4)



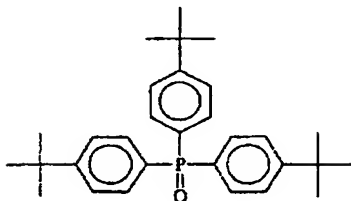
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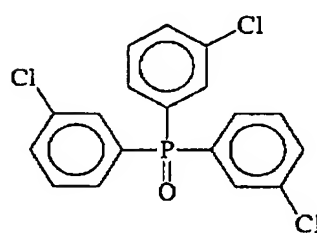
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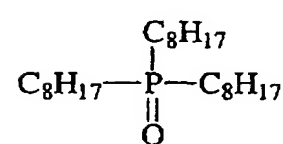
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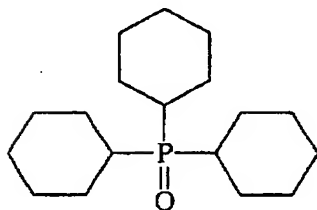
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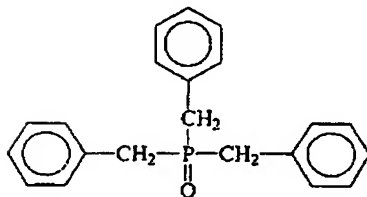
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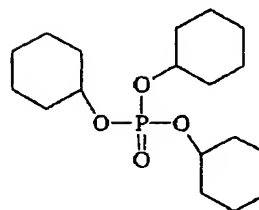
(D-10)



(D-11)



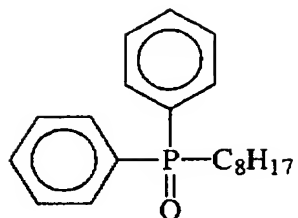
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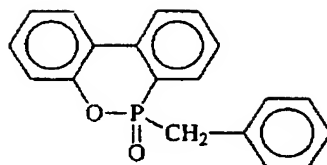
[0109]

[F8]

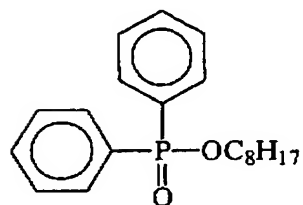
(D-13)



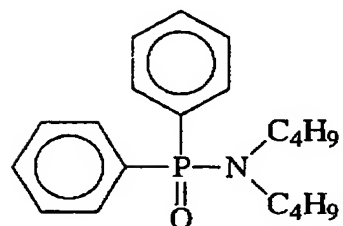
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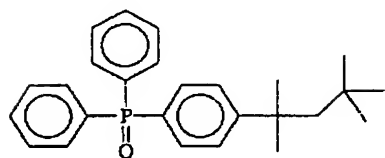
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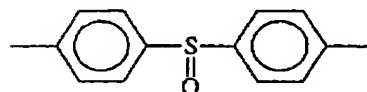
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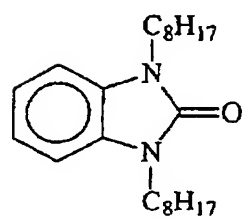
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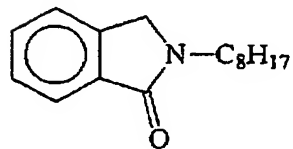
(D-18)



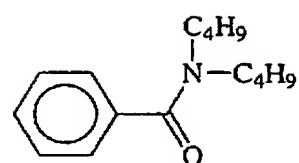
(D-19)



(D-20)



(D-21)



[0110]

In addition to the above listed, specific examples of hydrogen bond-forming compounds include those as described in Japanese Patent Application Nos. 2000-192191 and 2000-194811.

[0111]

The hydrogen bond-forming compound according to the invention may be incorporated in a coating solution, in the same manner as for the reducing agent, in any form selected from the group consisting of a solution, an emulsified dispersion and a solid fine particle dispersion, and thus contained in the photosensitive material. The hydrogen bond-forming compound according to the invention forms a complex in a solution state by forming a hydrogen bond with a compound having a phenolic hydroxyl group, whereby the complex, depending on combinations of the reducing agents and the compounds represented by the general formula (D) used in the invention, may be isolated as crystals.

[0112]

In order to exhibit a stable property, it is particularly preferable that the thus-isolated crystal powder is used as the solid fine particle dispersion. Further, preferably employed is a method in which the reducing agent and the hydrogen bond-forming compound according to the invention are mixed, each as a powder, and then dispersed using an appropriate dispersing agent utilizing a sand grinder mill or the like

to form a complex at the time of dispersing operation.

[0113]

The hydrogen bond-forming compound according to the invention is used, relative to the reducing agent, preferably in the range of from 1 mol% to 200 mol%, more preferably in the range of from 10 mol% to 150 mol% and still more preferably in the range of from 30 mol% to 100 mol%.

[0114]

#### 1-1-6. Binder

A binder contained in the layer containing the organic silver salt according to the invention may be any type of polymers. Suitable binder are transparent or semi-transparent and ordinarily colorless, and examples thereof include natural resins or polymers and copolymers, synthetic resins or polymers and copolymers, and other media for forming a film and examples thereof include gelatins, rubbers, polyvinyl alcohols, hydroxyethyl celluloses, cellulose acetates, cellulose acetate butyrates, polyvinyl pyrrolidones, casein, starch, polyacrylic acids, polymethyl methacrylic acids, polyvinyl chlorides, polymethacrylic acids, styrene/maleic acid anhydride copolymers, styrene/acrylonitrile copolymers, styrene/butadiene copolymers, polyvinyl acetals (e.g., polyvinyl formal and polyvinyl butyral), polyesters, polyurethanes, phenoxy resins, polyvinylidene chlorides, polyepoxides, polycarbonates, polyvinyl acetates, polyolefins, cellulose



esters and polyamides. Binders can be formed by being coated with water, organic solvents or emulsion of the binder.

[0115]

According to the invention, a glass transition temperature of the binder in the organic silver salt-containing layer is preferably in the range of from 10°C to 80°C, more preferably in the range of from 20°C to 70°C, and still more preferably in the range of from 23°C to 65°C.

[0116]

As used herein, T<sub>g</sub> is calculated according to the following equation:

$$1/T_g = \sum(X_i/T_{gi})$$

[0117]

The polymer whose glass transition point T<sub>g</sub> is calculated as above comprises n's monomers copolymerized (i indicates the number of the monomers copolymerized, falling between 1 and n); X<sub>i</sub> indicates the mass fraction of i'th monomer ( $\sum X_i = 1$ ); T<sub>gi</sub> indicates the glass transition point (in terms of the absolute temperature) of the homopolymer of i'th monomer alone; and  $\sum$  indicates the sum total of i falling between 1 and n.

Incidentally, the value of glass transition point (T<sub>gi</sub>) of the homopolymer of each monomer alone is adopted from the values described in "*Polymer Handbook*" (3rd Edition) (written by J. Brandrup,

E. H. Immergut (Wiley-Interscience, 1989)).

[0118]

A single kind of polymer may be used for the binder, or alternatively, two or more kinds of polymers may be used in combination. For example, a combination of a polymer having a glass transition point of higher than 20°C and another polymer having a glass transition point of lower than 20°C is possible. In case where at least two kinds of polymers that differ in T<sub>g</sub> are blended for use therein, it is desirable that the mass-average T<sub>g</sub> of the resulting blend falls within the ranges specified as above.

[0119]

In case where the organic silver salt-containing layer is formed by applying a coating solution in which at least 30 % by mass of the solvent is water, followed by drying, and in case where the binder to be included in the organic silver salt-containing layer is soluble or dispersible in an aqueous solvent (watery solvent), and especially when the binder to be included in the organic silver salt-containing layer is a polymer latex having an equilibrium water content of at most 2 % by mass at 25°C and 60% RH, the photothermographic material achieves improved properties. Most preferably, the binder for use in the present invention has ionic conductivity at most 2.5 mS/cm. In order to prepare such a binder, employable is a method of preparing a polymer followed by purification through a functional membrane for

separation.

[0120]

The aqueous solvent as used herein in which the polymer binder is soluble or dispersible in water or a mixture of water and at most 70 % by mass of a water-miscible organic solvent. The water-miscible organic solvent includes, for example, alcohols such as methyl alcohol, ethyl alcohol, propyl alcohol; cellosolves such as methyl cellosolve, ethyl cellosolve, butyl cellosolve; ethyl acetate, and dimethylformamide.

[0121]

The term "equilibrium water content at 25°C and 60% RH" as used herein is represented by the following equation, in which  $W^1$  indicates the mass of a polymer in humidity-conditioned equilibrium at 25°C and 60% RH, and  $W^0$  indicates the absolute dry mass of the polymer at 25°C.

Equilibrium water content at 25°C and 60% RH

$$= \{(W^1 - W^0)/W^0\} \times 100 \text{ (mass \%)}$$

For the details of the definition of water content and the method for measuring it, for example, referred to is "*Lecture of High Polymer Engineering*", No.14, Test Methods for High Polymer Materials (by the Society of High Polymer of Japan, Chijin Shokan).

[0122]

Preferably, the equilibrium water content at 25°C and 60% RH of the binder polymer for use in the present invention is at most 2 % by mass, more preferably from 0.01 to 1.5 % by mass, even more preferably from 0.02 to 1 % by mass.

[0123]

Polymers for use in the present invention are preferably dispersible in aqueous solvents. Preferable polymer dispersions include, for example, a polymer latex in which water-insoluble hydrophobic polymer microparticles are dispersed, a dispersion in which a molecular or micellar polymer is dispersed, and the like. Any of such a polymer dispersion is preferred for use in the present invention. The particles in the polymer dispersion preferably have a mean particle size falling between 1 and 50,000 nm, more preferably approximately between 5 and 1,000 nm. The particle size distribution of the dispersed particles is not specifically limited. For example, the dispersed particles may have a broad particle size distribution, or may have a monodispersed size distribution

[0124]

Preferable examples of polymers which are dispersible in an aqueous solvent for use in the present invention include hydrophobic polymers such as acrylic polymers, poly(esters), rubbers (e.g., SBR resins), poly(urethanes), poly(vinyl chlorides), poly(vinyl acetates), poly(vinylidene chlorides), and poly(olefins). These polymers may be

linear, branched or crosslinked. They may be homopolymers from a single monomer, or copolymers from two or more kinds of monomers. The copolymers may be random copolymers or block copolymers.

[0125]

The polymers preferably have a number-average molecular weight falling between 5,000 and 1,000,000, and more preferably between 10,000 and 200,000. If too small a molecular weight of polymer is used, the mechanical strength of the image-forming layer is insufficient; in contrast, if too large a molecular weight of polymer is used, film forming properties are poor.

[0126]

Preferred examples of polymer latex for use in the present invention are mentioned below. These polymer latexes are expressed by their constituent monomers, in which each numeral in parentheses indicates the proportion, in terms of % by mass, of the monomer unit, and the molecular weight of the constituent monomers represents the number-average molecular weight. When polyfunctional monomers are used, the molecular weights of the constituent monomers are omitted and only referred to as "crosslinked" in parentheses since the concept of molecular weight does not apply thereto. T<sub>g</sub> indicates the glass transition point of a polymer latex.

[0127]

- P-1; a latex (MW: 37,000; Tg: 61°C) of MMA(70)/EA(27)/MAA(3)
- P-2; a latex (MW: 40,000; Tg: 59°C) of MMA(70)/2EHA(20)/St(5)/AA(5)
- P-3; a latex (crosslinked; Tg: -17°C) of St(50)/Bu(47)/MAA(3)
- P-4; a latex (crosslinked; Tg: 17°C) of St(68)/Bu(29)/AA(3)
- P-5; a latex (crosslinked; Tg: 24°C) of St(71)/Bu(26)/AA(3)
- P-6; a latex (crosslinked) of St(70)/ Bu(27)/IA(3)
- P-7; a latex (crosslinked; Tg: 29°C) of St(75)/Bu(24)/AA(1)
- P-8; a latex (crosslinked) of St(60)/Bu(35)/DVB(3)/MAA(2)
- P-9; a latex (crosslinked) of St(70)/Bu(25)/DVB(2)/AA(3)
- P-10; a latex (MW: 80,000) of VC(50)/MMA(20)/EA(20)/AN(5)/AA(5)
- P-11; a latex (MW: 67,000) of VDC(85)/MMA(5)/EA(5)/MAA(5)
- P-12; a latex (MW: 12,000) of Et(90)/MAA(10)
- P-13; a latex (MW: 130,000; Tg: 43°C) of St(70)/2EHA(27)/AA(3)
- P-14; a latex (MW: 33,000; Tg: 47°C) of MMA(63)/EA(35)/AA(2)
- P-15; a latex (crosslinked; Tg: 23°C) of St(70.5)/Bu(26.5)/AA(3)
- P-16; a latex (crosslinked; Tg: 20.5°C) of St(69.5)/Bu(27.5)/AA(3)

[0128]

Abbreviations of constituent monomers are as follows:

MMA: methyl metacrylate; EA: ethyl acrylate; MAA: methacrylic acid;  
 2EHA: 2-ethylhexyl acrylate; St: Styrene; Bu: Butadiene; AA: acrylic  
 acid; DVB: divinyl benzene; VC: vinyl chloride; AN: acrylonitrile; VDC:  
 vinylidene chloride; Et: ethylene; and IA: itaconic acid.

[0129]

The polymer latexes mentioned above are commercially available. Some available products employable in the present invention are mentioned below. Examples of acrylic polymers include CEBIAN A-4635, 4718 and 4601 (produced by Daicel Chemical Industries), and NIPOL Lx811, 814, 821, 820 and 857 (produced by Nippon Zeon); examples of poly(esters) include FINETEX ES650, 611, 675 and 850 (produced by Dai-Nippon Ink & Chemicals), and WD-size and WMS (produced by Eastman Chemical); examples of poly(urethanes) include HYDRAN AP10, 20, 30 and 40 (produced by Dai-Nippon Ink & Chemicals); examples of rubbers include LACSTAR 7310K, 3307B, 4700H and 7132C (produced by Dai-Nippon Ink & Chemicals), and Nipol Lx416, 410, 438C and 2507 (produced by Nippon Zeon); examples of poly(vinyl chlorides) include G351 and G576 (produced by Nippon Zeon); examples of poly(vinylidene chlorides) include L502 and L513 (produced by Asahi Kasei); and examples of poly(olefins) include CHEMIPEARL S120 and SA100 (produced by Mitsui Petrochemical).

These polymer latexes may be used either singly or, as necessary, in combination of two or more.

[0130]

Particularly preferable polymer latex for use in the present invention is styrene/butadiene copolymer latex. In the styrene/butadiene copolymer, the ratio of styrene monomer unit to butadiene monomer unit preferably falls between 40:60 and 95:5 by

mass. Further, the proportion of styrene monomer unit and butadiene monomer unit preferably accounts for from 60 to 99 % by mass of the copolymer. The preferred range of the molecular weight of the copolymer is the same as described above.

[0131]

Preferred styrene/butadiene copolymer latexes for use in the present invention are the above-mentioned P-3 to P-8, P-14 and P-15, and commercially available products, LACSTAR-3307B, 7132C, and Nipol Lx416.

[0132]

The organic silver salt-containing layer of the photothermographic material of the present invention may optionally contain a hydrophilic polymer serving as a binder, such as gelatin, polyvinyl alcohol, methyl cellulose, hydroxypropyl cellulose and the like.

[0133]

The amount of the hydrophilic polymer to be included in the layer is preferably at most 30 % by mass, and more preferably at most 20 % by mass of the total binder in the organic silver salt-containing layer.

[0134]



It is preferable to use a polymer latex as the binder for forming the organic silver salt-containing layer (that is, the image-forming layer) of the photothermographic material of the present invention. Specifically, the binder is used in the organic silver salt-containing layer in a ratio of a total binder/an organic silver salt falling between 1/10 and 10/1, and more preferably between 1/5 and 4/1 by mass.

[0135]

The organic silver salt-containing layer is a photosensitive layer (an emulsion layer) which generally contains a photosensitive silver salt, that is, a photosensitive silver halide. In the layer, the ratio of total binder/silver halide preferably falls between 5 and 400, and more preferably between 10 and 200 by mass.

[0136]

The overall amount of the binder in the image-forming layer of the photothermographic material of the present invention preferably falls between 0.2 and 30 g/m<sup>2</sup>, and more preferably between 1 and 15 g/m<sup>2</sup>. The image-forming layer may optionally contain a crosslinking agent, and a surfactant for improving the coatability of the coating solution.

[0137]

According to the invention, a solvent (for the purpose of simplicity, a solvent and a dispersing medium are unanimously

expressed as solvent) of a coating solution for an organic silver salt-containing layer of the photosensitive material is preferably an aqueous solvent containing 30% by mass or more of water. As the components exclusive of water, any types of water-miscible organic solvents such as methyl alcohol, ethyl alcohol, isopropyl alcohol, Methyl Cellosolve, Ethyl Cellosolve, dimethyl formamide, and ethyl acetate may be used. A water content of such solvent is preferably 50% by mass or more, and more preferably 70% by mass or more.

[0138]

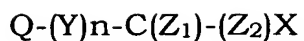
Examples of preferable solvent compositions include, taking a case of water=100 for granted, water/methyl alcohol=90/10, water/methyl alcohol=70/30, water/methyl alcohol/dimethyl formamide=80/15/5, water/methyl alcohol/Ethyl Cellosolve =85/10/5 and water/methyl alcohol/isopropyl alcohol=85/10/5 (numerical values being indicated in terms of "% by mass").

[0139]

#### 1-1-7. Fogging Inhibitor

According to the invention, it is preferable to contain any one of compounds which are represented by the following general formula (H) as the fogging inhibitor:

[0140]



GENERAL FORMULA (H)

[0141]

wherein Q represents an alkyl group, an aryl group or a heterocyclic group; Y represents a divalent linking group; n represents 0 or 1; Z<sup>1</sup> and Z<sup>2</sup> each independently represent a halogen atom; and X represents a hydrogen atom or an electron-attracting group.

[0142]

In the general formula (H), Q preferably represents a phenyl group substituted with an electron-attracting group having a positive Hammett's substituent constant  $\sigma_p$ . Regarding the Hammett's substituent constant, the *Journal of Medicinal Chemistry*, 1973, Vol. 16, No. 11, pp. 1207 to 1216 may be referred to.

[0143]

Examples of such electron-attracting groups include a halogen atom (e.g., a fluorine atom ( $\sigma_p$  value: 0.06)), a chlorine atom ( $\sigma_p$  value: 0.23), a bromine atom ( $\sigma_p$  value: 0.23) and an iodine atom ( $\sigma_p$  value: 0.18)), a trihalomethyl group (e.g., a tribromomethyl group ( $\sigma_p$  value: 0.29), a trichloromethyl group ( $\sigma_p$  value: 0.33) and a trifluoromethyl group ( $\sigma_p$  value: 0.54)), a cyano group ( $\sigma_p$  value: 0.66), a nitro group ( $\sigma_p$  value: 0.78), an aliphatic, aryl or a heterocyclic sulfonyl group (e.g., a methane sulfonyl group ( $\sigma_p$  value: 0.72)), an aliphatic, aryl or a heterocyclic acyl group (e.g., an acetyl group ( $\sigma_p$  value: 0.50) and a

benzoyl group ( $\sigma_p$  value: 0.43)), an alkynyl group (e.g., a group of  $C\equiv CH$  ( $\sigma_p$  value: 0.23)), an aliphatic, aryl or a heterocyclic oxycarbonyl group (e.g., a methoxycarbonyl group ( $\sigma_p$  value: 0.45) and a phenoxycarbonyl group ( $\sigma_p$  value; 0.44)), a carbamoyl group ( $\sigma_p$  value: 0.36), a sulfamoyl group ( $\sigma_p$  value: 0.57), a sulfoxide group, a heterocyclic group and a phosphoryl group.

A  $\sigma_p$  value is preferably in the range of from 0.2 to 2.0, and more preferably in the range of from 0.4 to 1.0.

[0144]

Particularly preferable electron-attracting groups are a carbamoyl group, an alkoxycarbonyl group, an alkylsulfonyl group, an alkylphosphoryl group, a carboxyl group, an alkyl- or aryl-carbonyl group, and an arylsulfonyl group. Particularly preferable groups are a carbamoyl group, an alkoxycarbonyl group, an alkylsulfonyl group, and an alkylphosphoryl group. Most preferable group is a carbamoyl group.

[0145]

X is preferably an electron-attracting group, and more preferably a halogen atom, an aliphatic, aryl or a heterocyclic sulfonyl group, an aliphatic, aryl or a heterocyclic acyl group, an aliphatic, aryl or a heterocyclic oxycarbonyl group, a carbamoyl group or a sulfamoyl group. A halogen atom is particularly preferred.

Among the halogen atoms, a chlorine atom, a bromine atom

and an iodine atom are preferable; a chlorine atom and a bromine atom are more preferable; and a bromine atom is particularly preferable.

[0146]

In the general formula (H), Y preferably represents -C(=O)-, -SO- or -SO<sub>2</sub>- , with -C(=O)- or -SO<sub>2</sub>- being more preferable, and -SO<sub>2</sub>- being particularly preferable. n represents 0 or 1, with 1 being preferable.

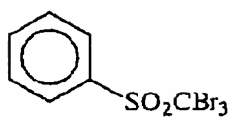
[0147]

Specific examples of compounds represented by the general formula (H) according to the invention are listed below; however, the invention is not limited thereto.

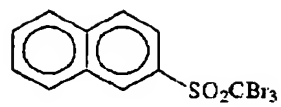
[0148]

[F19]

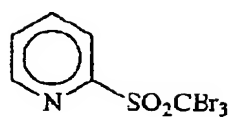
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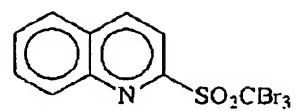
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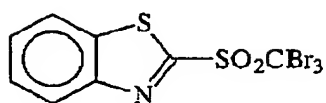
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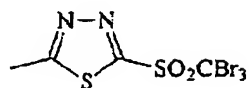
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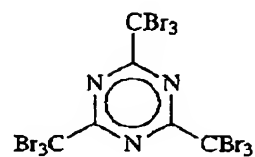
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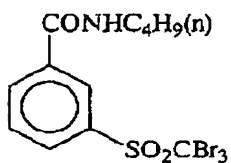
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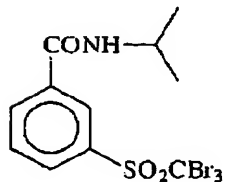
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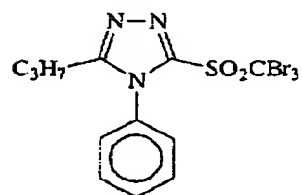
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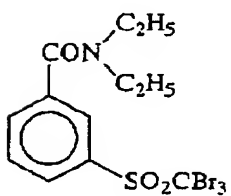
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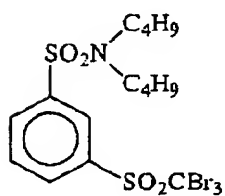
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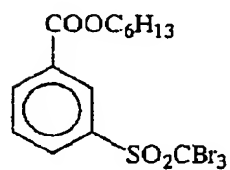
(H-11)



(H-12)



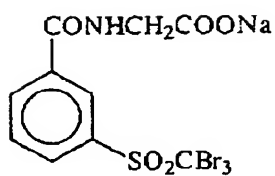
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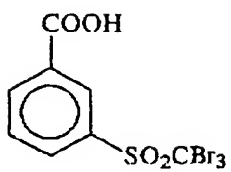
[0149]

[F10]

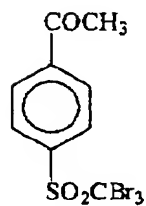
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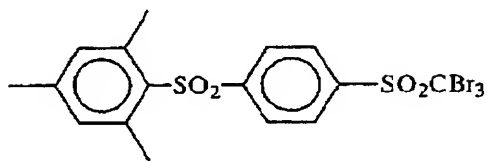
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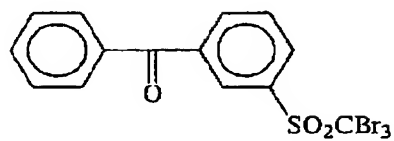
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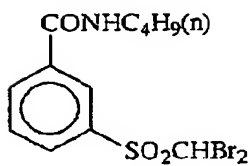
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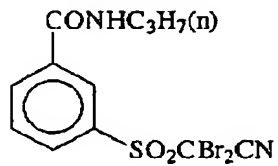
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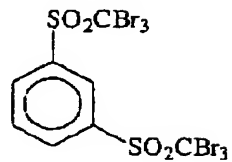
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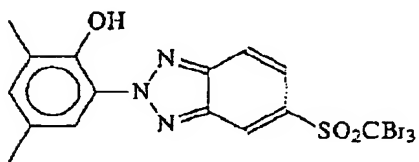
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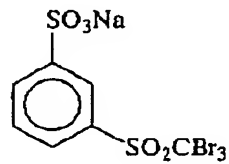
(H-21)



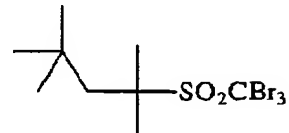
(H-22)



(H-23)



(H-24)



[0150]

The compound represented by the general formula (H) according to the invention is used, per mol of non-photosensitive silver salt in the image-forming layer, preferably in the range of from  $1 \times 10^{-4}$  mol to 0.8 mol, more preferably in the range of from  $1 \times 10^{-3}$  mol to 0.1 mol, and still more preferably in the range of from  $5 \times 10^{-3}$  mol to 0.05 mol.

Particularly in the case where the silver halide having a composition in which a silver iodide content is high according to the present invention is used, an addition amount of the compound represented by the general formula (H) is a critical factor so as to obtain a sufficient antifogging effect, and the compound is most preferably used in an amount ranging from  $5 \times 10^{-3}$  mol to 0.03 mol.

[0151]

As the methods for incorporating the compound represented by the general formula (H) according to the invention in the photosensitive material, the same methods as those described for the reducing agent are applicable.

[0152]

A melting point of the compound represented by the general formula (H) is preferably 200°C or lower and more preferably 170°C or lower.

[0153]



As other organic polyhalogen compounds for use in the invention, compounds set forth in paragraphs [0111] to [0112] of JP-A No. 11-65021 are mentioned. In particular, organic halides represented by the formula (P) in Japanese Patent Application No. 11-87297, organic polyhalogen compounds represented by the general formula (II) in JP-A No. 10-339934 and organic polyhalogen compounds described in Japanese Patent Application No. 11-205330 are preferable.

[0154]

#### 1-1-8. Other Fogging Inhibitors

As other fogging inhibitors, a mercury (II) salt as described in paragraph [0113] of JP-A No. 11-65021, benzoic acids as described in paragraph [0114] of P-A No. 11-65021, a salicylic acid derivative as described in JP-A No. 2000-206642, a formalin scavenger compound represented by the formula (S) in JP-A No. 2000-221634, a triazine compound stated in claim 9 of JP-A No. 11-352624, compounds represented by the general formula (III) of JP-A No. 6-11791, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and the like are used in the invention.

[0155]

As the fogging inhibitor, stabilizer and stabilizer precursor, those described in paragraph [0070] of JP-A No. 10-62899, pp. 20 (line 57) to 21 (line 7) of EP-A No. 0803764, and compounds described in

JP-A Nos. 9-281637 and 9-329864 are used in the invention.

[0156]

The photothermographic material according to the invention may contain an azolium salt for the purpose of inhibiting fogging. As the azolium salt, compounds represented by the general formula (XI) as described in JP-A No. 59-193447, compounds as described in JP-B No. 55-12581, and compounds represented by the general formula (II) as described in JP-A No. 60-153039 may be used. The azolium salt may be added in any portion of the photosensitive material; however, as the layer to be added with the azolium salt, the layer at a surface having the photosensitive layer is preferable, and the layer containing the organic silver salt is more preferable.

[0157]

Addition of the azolium salt may be conducted in any step for preparing a coating solution. When the azolium salt is added to the layer containing the organic silver salt, the azolium salt may be added in any step of from preparation of the organic silver salt to preparation of a coating solution; however, the azolium salt is preferably added during a period of after the preparation of the organic silver salt to immediately before the coating. In order to add the azolium salt, any addition method, such as that in a powder state, a solution state or a fine particle dispersion state thereof, may be adopted. The azolium salt may also be added in a state of solution mixed with other additives

such as a sensitizing dye, a reducing agent and a toning agent.

[0158]

According to the invention, an addition amount of the azolium salt may be arbitrary; however, it is preferably in the range of from  $1 \times 10^{-6}$  mol to 2 mol, and more preferably in the range of from  $1 \times 10^{-3}$  mol to 0.5 mol, per mol of silver.

[0159]

#### 1-1-9. Other Additives

##### 1) Mercapto, Disulfide and Thiones

According to the invention, in order to control development by inhibiting or accelerating the development, improve spectral sensitizing efficiency, improve storability before and after the development, a mercapto compound, a disulfide compound or a thione compound can be incorporated. Compounds as described in paragraphs [0067] to [0069] of JP-A No. 10-62899, compounds represented by the general formula (I) and their specific examples as described in paragraphs [0033] to [0052] of JP-A No. 10-186572, compounds described in page 20, lines 36 to 56 of EP-A No. 0803764, and compounds as described in Japanese Patent Application No. 11-273670 may be mentioned.

[0160]

##### 2) Toning Agent

In the photothermographic material according to the invention,

a toning agent is preferably included. Such toning agents are described in paragraphs [0054] to [0055] of JP-A No. 10-62899, page 21, lines 23 to 48 of EP-A No. 0803764, JP-A No. 2000-356317 and Japanese Patent Application No. 2000-187298. In particular, phthalazinones (phthalazinone, phthalazinone derivatives or their metal salts, e.g., 4-(1-naphthyl)phthalazinone, 6-chlorophthalazinone, 5,7-dimethoxy phthalazinone and 2,3-dihydro-1,4-phthalazinedione); combinations of phthalazinones and phthalic acids (e.g., phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid, diammonium phthalate, sodium phthalate, potassium phthalate and tetrachlorophthalic acid anhydride); phthalazines (phthalazine, phthalazine derivatives or their metal salts, e.g., 4-(1-naphthyl)phthalazine, 6-isopropylphthalazine, 6-t-butylphthalazine, 6-chlorophthalazine, 5,7-dimethoxyphthalazine and 2,3-dihydrophthalazine) are preferable. When combined with a silver halide having a composition whose silver iodide content is high, a combination of phthalazines and phthalic acids are particularly preferred.

[0161]

An addition amount of the phthalazines is, per mol of the organic silver salt, preferably in the range of from 0.01 mol to 0.3 mol, more preferably in the range of from 0.02 mol to 0.2 mol, and particularly preferably in the range of from 0.02 mol to 0.1 mol. Such addition amounts are critical factors to accelerate development, which is a concern of a silver halide emulsion disclosed herein, having a

composition whose silver iodide content is high. If appropriate addition amounts thereof are employed, sufficient development and lowered fogging are both achieved

[0162]

### 3) Plasticizer and Lubricant

Plasticizers and lubricants employable in the photosensitive layer according to the invention are described in paragraph [0117] of JP-A No. 11-65021. Slipping agents are described in paragraphs [0061] to [0064] of JP-A No. 11-84573, and paragraphs [0049] to [0062] of Japanese Patent Application No. 11-106881.

[0163]

### 4) Dye and Pigment

In order to improve tones, prevent an interference fringe pattern to be generated by laser light exposure, and prevent irradiation, various types of dyes and pigments (e.g., C. I. Pigment Blue 60, C. I. Pigment Blue 64, and C. I. Pigment Blue 15:6) may be included in the photosensitive layer according to the invention. These dyes and pigments are detailed, for example, in WO98/36322, JP-A No. 10-268465, and 11-338098.

[0164]

### 5) Ultra-high Contrast Agent

In order to form ultra-high contrast images applied for a

printing plate fabrication, an ultra-high contrast agent is preferably included in an image-forming layer. As the ultra-high contrast agents, adding methods thereof, and respective addition amounts are described in paragraph [0118] of JP-A No. 11-65021, and paragraphs [0136] to [0193] of JP-A No. 11-223898, compounds represented by the formula (H), the formulas (1) to (3) and the formulas (A) and (B) in Japanese Patent Application No. 11-87297, and compounds represented by the general formulas (III) to (V) in Japanese Patent Application No. 11-91652 (specifically, compounds denoted as Chemicals 21 to 24). Also, high contrast promoting agents are described in paragraph [0102] of JP-A No. 11-65021, and paragraph [0194] to [0195] of JP-A No. 11-223898.

[0165]

When formic acid or a salt thereof is used as a strong fogging agent, it may be added to a side provide with the image-forming layer containing the photosensitive silver halide in an amount, per mol of silver, preferably of 5 mmol or less, and more preferably of 1 mmol or less.

When the ultra-high contrast agent is used in the photothermographic material according to the invention, it is preferable to use the agent in combination with an acid or a salt thereof formed through hydration of phosphorus pentaoxide. As the acid or the salt thereof formed through hydration of phosphorus pentoxide, mentioned are metaphosphoric acid (and salts thereof),

pyrophosphoric acid (and salts thereof), orthophosphoric acid (and salts thereof), triphosphoric acid (and salts thereof), tetraphosphoric acid (and salts thereof) and hexametaphosphoric acid (and salts thereof). Acids formed through hydration of phosphorus pentoxide or the salts thereof which are particularly preferably used are orthophosphoric acid (and salts thereof) and hexametaphosphoric acid (and salts thereof). Specific examples of the salts include sodium orthophosphate, sodium dihydrogen orthophosphate, sodium hexametaphosphate and ammonium hexametaphosphate.

An amount of the acid formed through hydration of phosphorus pentoxide or the salt thereof to be used (in terms of a coating amount based on 1 m<sup>2</sup> of the photosensitive material) may be a desired quantity, depending on properties of sensitivity, fog, and the like; however, it is preferably in the range of from 0.1 mg/m<sup>2</sup> to 500 mg/m<sup>2</sup>, and more preferably in the range of from 0.5 mg/m<sup>2</sup> to 100 mg/m<sup>2</sup>.

[0166]

#### 1-1-10. Preparation and Application of Coating Solution

A temperature at which the coating solution for the image-forming layer according to the invention is prepared is preferably in the range of from 30°C to 65°C, more preferably from 35°C to 60°C, and still more preferably from 35°C to 55°C. It is also preferable that the temperature of the coating solution for the image-forming layer immediately after addition of the polymer latex is maintained in the range of from 30°C to 65°C.

[0167]

## 1-2. Other Layers, and Components thereof

The photothermographic material according to the invention may have a non-photosensitive layer, in addition to the image-forming layer. The non-photosensitive layer may be divided depending on its disposition into the following; (a) a surface protective layer formed on the image-forming layer (on a position remote from the support), (b) an intermediate layer formed between any two of a plurality of image-forming layers or between the image-forming layer and the protective layer, (c) an undercoat layer formed between the image-forming layer and the support, and (d) a back layer formed on an opposite side of the image-forming layer.

[0168]

Further, a layer acting as an optical filter may be provided in the photosensitive material as a layer of the above-described (a) or (b). An antihalation layer may be formed in the photosensitive material as a layer of the above-described (c) or (d).

[0169]

### 1) Surface Protective Layer

The photothermographic material according to the invention may have a surface protective layer for the purpose of preventing adhesion of the image-forming layer. The surface protective layer may



be of a monolayer or of a multilayer. Such surface protective layers are described in paragraphs [0119] to [0120] of JP-A No. 11-65021, and Japanese Patent Application No. 2000-171936.

[0170]

As the binder used for the surface protective layer according to the invention, gelatin is preferably used. Also, polyvinyl alcohol (PVA) is preferably used solely or in combination with gelatin. As gelatin, inert gelatin (e.g., Nitta Gelatin 750), phthalated gelatin (e.g., Nitta Gelatin 801) and the like may be used.

[0171]

As PVA, those described in paragraphs [0009] to [0020] of JP-A No. 2000-171936 may be used. PVA-105 as a completely saponified PVA, PVA-205 and PVA-335 as a partly saponified PVA, and MP-203 as a modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd.) are preferably used.

[0172]

A coating amount (based on 1 m<sup>2</sup> of the support) of polyvinyl alcohol in the protective layer (for one layer) is preferably in the range of from 0.3 g/m<sup>2</sup> to 4.0 g/m<sup>2</sup>, and more preferably in the range of from 0.3 g/m<sup>2</sup> to 2.0 g/m<sup>2</sup>.

[0173]

A coating amount (based on 1 m<sup>2</sup> of the support) of the entire binder (including water-soluble polymer and latex polymer) in the surface protective layer (for one layer) is preferably in the range of from 0.3 g/m<sup>2</sup> to 5.0 g/m<sup>2</sup>, and more preferably in the range of from 0.3 g/m<sup>2</sup> to 2.0 g/m<sup>2</sup>.

[0174]

## 2) Antihalation Layer

In the photothermographic material according to the invention, an antihalation layer may be provided at a side distant from a light source relative to the photosensitive layer. Such antihalation layers are described, for example, in paragraphs [0123] to [0124] of JP-A No. 11-65021, JP-A Nos. 11-223898, 9-230531, 10-36695, 10-104779, 11-231457, 11-352625 and 11-352626.

[0175]

The antihalation layer contains an antihalation dye capable of absorbing light in a range of wavelengths of light for exposing the photothermographic material. When such a wavelength is in an infrared region, a dye absorbing an infrared ray may be used; on this occasion, the dye which do not absorb visible light is used.

[0176]

When antihalation is performed using a dye capable of absorbing visible light, it is preferred that color of the dye are rendered

substantially decolored after image formation, by employing a device to decolorize the dye by heat generated by thermal development. It is particularly preferable to add a thermally decolorizable dye and a base precursor to the non-photosensitive layer to make the resultant non-photosensitive layer to function as an antihalation layer. Such techniques are described, for example, in JP-A No. 11-231457.

[0177]

An addition amount of the decolorizable dye is determined depending on the use purpose of the dye. Ordinarily, the decolorizable dye is used in such an amount to obtain an optical density (absorbance) measured at a predetermined wavelength exceeding 0.1. The optical density is preferably in the range of from 0.2 to 2. The use amount of the decolorizable dye to obtain the desired optical density is usually in the range of from about 0.001 g/m<sup>2</sup> to about 1 g/m<sup>2</sup>.

[0178]

If the dyes are decolorized in such a manner, the optical density can be lowered to 0.1 or less after thermal development. Two or more types of decolorizable dyes may be used in combination in a thermally decolorizable-type recording material or in the photothermographic material. In a similar way, two or more types of base precursors may be used in combination.

[0179]

When thermally decoloring is conducted using such a decolorizable dye and base precursor, it is preferable from the viewpoint of thermal decolorability to use a substance which, when used in combination with the base precursor, can lower the melting point by at least 3°C (e.g., diphenylsulfone or 4-chlorophenyl(phenyl)sulfone), as described in JP-A No. 11-352626.

[0180]

### 3) Back layer

As to a back layer which is applicable to the invention, descriptions are found in paragraphs [0128] to [0130] of JP-A No. 11-65021.

[0181]

According to the invention, a coloring agent having an absorption maximum in a wavelength region of from 300 nm to 450 nm can be added for the purposes of enhancing a silver color tone and improving a change in an image with time. Such coloring agents are described in JP-A Nos. 62-210458, 63-104046, 63-103235, 63-208846, 63-306436, 63-314535, 1-61745, Japanese Patent Application No. 11-276751, etc. These coloring agents are usually added in an amount in a range of from 0.1 mg/m<sup>2</sup> to 1 g/m<sup>2</sup>. As to a layer for the agent to be added to, the back layer provided on an opposite side of the photosensitive layer is preferable.

[0182]

#### 4) Matting Agent

According to the invention, it is preferable to add a matting agent to the surface protective layer and the back layer for the purpose of improving a transportation property. Such matting agents are described in paragraphs [0126] and [0127] of JP-A No. 11-65021.

A coating amount of the matting agent is preferably in a range of from 1 mg/m<sup>2</sup> to 400 mg/m<sup>2</sup>, and more preferably from 5 mg/m<sup>2</sup> to 300 mg/m<sup>2</sup> per m<sup>2</sup> of the photothermographic material.

[0183]

A matte degree of an emulsion surface is not particularly limited so far as a so-called star dust-like defect, in which a small blank area is generated in an imaged portion to cause light leaks, does not occur. However, a Beck's smoothness is preferably in a range of from 30 seconds to 2,000 seconds and particularly preferably in a range of from 40 seconds to 1,500 seconds. The Beck's smoothness may easily be obtained according to "Testing Method for Smoothness of Paper and Paperboard with Beck's Tester", the Japanese Industrial Standards (JIS) P8119 and the TAPPI Standard Method T479.

[0184]

According to the invention, the Beck's smoothness as a matte degree for the back layer is preferably in a range of from 10 seconds to

1,200 seconds, more preferably from 20 seconds to 800 seconds, and still more preferably from 40 seconds to 500 seconds.

[0185]

According to the invention, the matting agent is preferably contained in an outermost surface layer, a layer which functions as the outermost surface layer of the photothermographic material, a layer in the vicinity of an outer surface layer or a layer which functions as the so-called protective layer.

[0186]

#### 5) Polymer Latex

A polymer latex can be added to the surface protective layer and the back layer.

Such polymer latexes are described in "*Synthetic Resin Emulsion*", compiled by Taira Okuda and Hiroshi Inagaki, Kobunshi Kankokai (Polymer Publishing), 1978, "*Application of Synthesized Latex*", compiled by Takaaki Sugimura, Yasuo Kataoka, Soichi Suzuki and Keiji Kasahara, Kobunshi Kankokai (Polymer Publishing), 1993, Soichi Muroi, "*Chemistry of Synthesized Latex*", Kobunshi Kankokai (Polymer Publishing), 1970 and the like. Specific examples of the polymer latexes include a latex of a methyl methacrylate (33.5% by mass)/ethyl acrylate (50% by mass)/methacrylic acid (16.5% by mass) copolymer, a latex of a methyl methacrylate (47.5% by mass)/butadiene (47.5% by mass)/itaconic acid (5% by mass)

copolymer, a latex of an ethyl acrylate/methacrylic acid copolymer, a latex of a methyl methacrylate (58.9% by mass)/2-ethylhexyl acrylate (25.4% by mass)/styrene (8.6% by mass)/2-hydroxyethyl metacrylate (5.1% by mass)/acrylic acid (2.0% by mass) copolymer, and a latex of a methyl methacrylate (64.0% by mass)/styrene (9.0% by mass)/butylacrylate (20.0% by mass)/2-hydroxyethyl metacrylate (5.0% by mass)/acrylic acid (2.0% by mass) copolymer.

[0187]

The polymer latex is used in an amount, based on the entire binder in the surface protective layer or the back layer, of preferably from 10% by mass to 90% by mass, and particularly preferably from 20% by mass to 80% by mass.

[0188]

#### 6) Film Surface pH

In the photothermographic material according to the invention, a pH of a film surface before thermal development is preferably 7.0 or less, and more preferably 6.6 or less. A lower limit thereof is not particularly limited, but is approximately 3. A most preferable pH range is from 4 to 6.2.

[0189]

For adjusting the pH of the film surface, it is preferable from the viewpoint of lowering the pH of the film surface to use an organic acid

such as a phthalic acid derivative, a non-volatile acid such as sulfuric acid or a volatile base such as ammonia. Particularly, ammonia is preferable in achieving a low pH of the film surface, because ammonia is particularly volatile and may be removed during a coating process or before thermal development.

It is also preferable that a non-volatile base such as sodium hydroxide, potassium hydroxide or lithium hydroxide is used together with ammonia. Measuring methods of the pH of the film surface are described in paragraph [0123] of Japanese Patent Application No. 11-87297.

[0190]

#### 7) Hardening Agent

A hardening agent may be used in each of the photosensitive layer, the protective layer, the back layer and the like according to the invention.

Examples of such hardening agents employable are found in various methods described in T. H. James, *"The Theory of the Photographic Process"*, 4th edition, pp. 77 to 87, Macmillan Publishing Co., Inc., 1977. Other preferable examples of the hardening agents include not only chrome alum, a sodium salt of 2,4-dichloro-6-hydroxy-s-triazine, N,N-ethylene bis(vinylsulfonacetamide) and N,N-propylene bis(vinylsulfonacetamide), but also multivalent metal ions described in the above literature, pp. 78, polyisocyanates described in U.S. Patent No. 4,281,060 and JP-A



No. 6-208193, epoxy compounds described in U.S. Patent No. 4,791,042 and vinyl sulfone type compounds described in JP-A No. 62-89048.

[0191]

The hardening agent is added in the form of a solution. Addition of a hardening agent solution to the coating liquid for the protective layer is conducted during a time period of from 180 minutes before a coating operation to immediately before the coating operation, and preferably from 60 minutes before a coating operation to 10 seconds before the coating operation, and mixing methods and mixing conditions of the hardening agent solution are not particularly limited so far as the effects of the invention are sufficiently exerted.

[0192]

Specific examples of the mixing methods include a mixing method using a tank in which an average dwell time calculated from an addition flow rate and a feeding flow rate to a coater is specified to be a desired time and a mixing method using a static mixer or the like described in N. Harnby, M. F. Edwards and A. W. Nienow, *“Techniques of Mixing Liquids”*, translated by Koji Takahashi, Chapter 8, Nikkan Kogyo Newspaper, 1989.

[0193]

8) Surfactant

Surfactants applicable to the invention are described in paragraph [0132] of JP-A No. 11-65021.

According to the invention, it is preferable to use a fluorine-based surfactant. As specific examples of such surfactants, mentioned are compounds described in JP-A Nos. 10-197985, 2000-19680, 2000-214554 and the like. A polymeric fluorine-based surfactant described in JP-A No. 9-281636 is also preferably used. In the photothermographic material according to the invention, fluorine-based surfactants described in Japanese Patent Application Nos. 2000-206560 are preferably used.

[0194]

#### 9) Anti-Static Agent

In the invention, an anti-static layer comprising any one of electrically conductive materials such as various types of known metal oxides and electrically conductive polymers may be contained. The anti-static layer may be provided on any of an image-forming layer side and a back layer side, such that the anti-static layer may simultaneously serve as the above-described undercoat layer, back layer, protective layer or the like or may be provided separately from these layers. Preferably, the anti-static layer is provided between the support and the back layer. As for the anti-static layer, techniques described in paragraph [0135] of JP-A No. 11-65021, JP-A Nos. 56-143430, 56-143431, 58-62646 and 56-120519, paragraphs [0040] to [0051] of JP-A No. 11-84573, U.S. Patent No. 5,575,957, paragraphs

[0078] to [0084] of JP-A No. 11-223898 are employable.

[0195]

10) Support

As a transparent support, a polyester, in particular, polyethylene terephthalate, which has been thermally treated in a temperature range of from 130°C to 185°C in order to relax residual internal stress in a film at the time of biaxially stretching and to eliminate stress of thermal contraction generated in thermal development, is preferably used.

[0196]

In a case of the photothermographic material for medical use, the transparent support may be colored with blue dyes (for example, Dye-1 described in JP-A No. 8-240877) or may remain colorless.

Specific examples of such supports are described in paragraph [0134] of JP-A No. 11-65021.

[0197]

To the support, undercoating techniques using a water-soluble polyester described in JP-A No. 11-84574, a styrene/butadiene copolymer described in JP-A No. 10-186565, vinylidene chloride copolymers described in JP-A No. 2000-39684 and paragraphs [0063] to [0080] of Japanese Patent Application No. 11-106881 and the like are preferably adopted.

[0198]

#### 11) Other Additives

To the photothermographic material, an anti-oxidant, a stabilizing agent, a plasticizer, a UV absorbent or a covering aid may further be added. A solvent described in paragraph [0133] of JP-A No. 11-65021 may also be added thereto. These various additives are included in either the photosensitive layer or the non-photosensitive layer. Concerning these matters, references may be made to WO98/36322, EP-A No. 803764, JP-A Nos. 10-186567, 10-18568 and the like.

[0199]

#### 12) Coating Method

The photothermographic material according to the invention may be coated by any method. Specifically, various types of coating methods including extrusion coating, slide coating, curtain coating, dip coating, knife coating, flow coating, and extrusion coating using a type of hopper described in U.S. Patent No. 2,681,294 are employed. Extrusion coating described in Stephen F. Kistler and Peter M. Schweizer, *"Liquid Film Coating"*, pp. 399 to 536, Chapman & Hall, 1997 or slide coating is preferably used. In particular, the slide coating is preferably used.

[0200]

Examples of shapes of slide coaters used for the slide coating are described in the above book, page 427, FIG. 11b-1. As desired, two or more layers can simultaneously be coated by methods described in the above book, pp. 399 to 536, U.S. Patent No. 2,761,791 and British Patent No. 837,095.

[0201]

The coating liquid for the organic silver salt-containing layer according to the invention is preferably a so-called thixotropic fluid. As to the techniques for such a thixotropic fluid, JP-A No. 11-52509 may be referred to.

In the present invention, the viscosity of the coating liquid for the organic silver salt-containing layer under a shearing velocity of  $0.1 \text{ S}^{-1}$  is preferably in a range of from 400 mPa·s to 100,000 mPa·s, and more preferably in a range of from 500 mPa·s to 20,000 mPa·s.

The viscosity under a shearing velocity of  $1,000 \text{ S}^{-1}$  is preferably in a range of from 1 mPa·s to 200 mPa·s, and more preferably in a range of from 5 mPa·s to 80 mPa·s.

[0202]

It is preferable that the photothermographic material according to the invention is subjected to a thermal treatment immediately after drying the coatings. Particularly, in a case of the photothermographic material in which a water-based latex is used as the binder, film strength is enhanced by the thermal treatment and handling of the

photothermographic material may be readily conducted. A temperature of the thermal treatment is, in terms of effective film surface temperature, preferably in the range of from 60°C to 100°C while a time period of heating is preferably in the range of from 1 second to 60 seconds. The conditions are more preferably in the range of from 70°C to 90°C and in the range of from 2 seconds to 10 seconds, respectively. A preferable heating method according to the invention can be referred to those as described in JP-A No. 2002-107872.

[0203]

### 13) Packaging Material

It is preferable that the photothermographic material according to the invention is seal-packed by a packaging material imparted with at least one property of low oxygen permeability and/or low moisture permeability, in order to prevent a photographic property thereof from being deteriorated during a storage period before being put in actual use or, in a case in which an end-product is in a roll state, to prevent the photothermographic material from being curled or being imparted with a winding crimp. The oxygen permeability at 25°C is preferably less than 50 ml/atm/m<sup>2</sup>·day, more preferably less than 10 ml/atm/m<sup>2</sup>·day, and still more preferably less than 1.0 ml/atm/m<sup>2</sup>·day. The moisture permeability is preferably less than 10 g/atm/m<sup>2</sup>·day, more preferably less than 5 g/atm/m<sup>2</sup>·day, and still more preferably less than 1 g/atm/m<sup>2</sup>·day. As specific examples of such packaging

materials imparted with at least one property of low oxygen permeability and/or low moisture permeability, those described in JP-A Nos. 8-254793 and 2000-206653 are employable.

[0204]

#### 14) Other Usable Techniques

As to techniques usable in the photothermographic material according to the invention, such techniques as described in the following references are further employed: EP-A Nos. 803764 and 883022, WO98/36322, JP-A Nos. 56-62648, 58-62644, 9-43766, 9-281637, 9-297367, 9-304869, 9-311405, 9-329865, 10-10669, 10-62899, 10-69023, 10-186568, 10-90823, 10-171063, 10-186565 and 10-186567, from JP-A No. 10-186569 to JP-A No. 10-186572, JP-A Nos. 10-197974, 10-197982 and 10-197983, from JP-A No. 10-197985 to JP-A No. 10-197987, JP-A Nos. 10-207001, 10-207004, 10-221807, 10-282601, 10-288823, 10-288824, 10-307365, 10-312038, 10-339934, 11-7100, 11-15105, 11-24200, 11-24201, 11-30832, 11-84574, 11-65021, 11-109547, 11-125880 and 11-129629, from JP-A No. 11-133536 to JP-A No. 11-133539, JP-A Nos. 11-133542, 11-133543, 11-223898, 11-352627, 11-305377, 11-305378, 11-305384, 11-305380, 11-316435, 11-327076, 11-338096, 11-338098, 11-338099 and 11-343420, Japanese Patent Application Nos. 2000-187298, 2000-10229, 2000-47345, 2000-206642, 2000-98530, 2000-98531, 2000-112059, 2000-112060, 2000-112104, 2000-112064 and 2000-171936.

[0205]

#### 15) Color Image Formation

A multi-color photothermographic material may comprise a combination of at least two layers of different colors or may comprise one layer containing all colors therein as described in U.S. Patent No. 4,708,928.

In a case of the multi-color photothermographic material, respective emulsion layers are, as described in U.S. Patent No. 4,460,681, ordinarily maintained in a separate manner from one another via a functional or non-functional barrier layer disposed between the respective photosensitive layers.

[0206]

#### 2. Image-Forming Method

##### 2-1. Exposure

The photothermographic material according to the present invention can be exposed in any manner. Preferably, laser light is used as a light source.

The silver halide emulsion having a high silver iodide content according to the invention has conventionally posed a problem in that sensitivity is low. However, it was found that the problem of such low sensitivity is solved by performing writing-in by means of such an intense irradiation using laser light whereby image recording can be performed by a smaller energy than conventional means. Thus,



desired sensitivity can be attained using strong intensity light in a short period of time.

[0207]

Particularly when a quantity of exposure which realizes a maximum density ( $D_{\max}$ ) is provided, a quantity of light on a surface of the photosensitive material is preferably in the range of from 0.1 W/mm<sup>2</sup> to 100 W/mm<sup>2</sup>, more preferably in the range of from 0.5 W/mm<sup>2</sup> to 50 W/mm<sup>2</sup>, and most preferably in the range of from 1 W/mm<sup>2</sup> to 50 W/mm<sup>2</sup>.

[0208]

The laser light for use in the present invention is, for example, gas laser ( $\text{Ar}^+$ , He-Ne or He-Cd), YAG laser, dye laser, or semiconductor laser. Also employable is a combination of a semiconductor laser and a secondary harmonic generating element. Laser to be preferably used is selected corresponding to a light absorption peak wavelength of, for example, a spectral sensitizing dye in the photothermographic material, but preferably is the He-Ne laser or a red color semiconductor laser which emits red to infrared light, or the  $\text{Ar}^+$  laser, the He-Ne laser, the He-Cd laser or a blue color semiconductor laser which emits blue to green light. In recent years, particularly, a module fabricated by unifying SHG (Second Harmonic Generator) element with the semiconductor laser, or the blue semiconductor laser has been developed, thereby rapidly attracting people's attention to a laser

output device in a short wavelength region. Since the blue semiconductor laser is capable of performing ultra-fine image recording, increasing a recording density and obtaining a long-life and consistent output, it is expected that demand for the blue semiconductor laser will be increased. The peak wavelength of the laser light is, in terms of blue color, in the range of from 300 nm to 500 nm, and preferably in the range of from 400 nm to 500 nm whereas, in terms of red to infrared, in the range of from 600 nm to 900 nm, and preferably in the range of from 620 nm to 850 nm.

[0209]

Laser light which oscillates in a longitudinal multi-mode by a method such as high frequency superimposition is preferably employed.

[0210]

## 2-2. Thermal Development

The photothermographic material according to the invention may be developed by any method. Ordinarily, a temperature of the photothermographic material which has been exposed image-wise is elevated to allow it to be developed. A development temperature is preferably in a range of from 80°C to 250°C, and more preferably in a range of from 100°C to 140°C. The development time period is preferably from 1 second to 60 seconds, more preferably from 5 seconds to 30 seconds, and still more preferably from 5 seconds to 20

seconds.

[0211]

As to a thermal development system, a plate heater system is preferably used. As to the thermal development system utilizing the plate heater system, methods described in JP-A No. 11-133572 are preferable, in which there is provided a thermal development apparatus that obtains a visible image by allowing a photothermographic material in which a latent image has been formed to contact with a heating unit in a thermal development portion thereof, wherein the thermal development apparatus is characterized in that the heating unit comprises a plate heater, a plurality of pressure rolls are provided along one surface of the plate heater such that the pressure rolls face to the plate heater and the thermal development is performed by allowing the photothermographic material to pass through between the pressure rolls and the plate heater. It is preferable that the plate heater is divided into 2 to 6 steps and that the top portion has a temperature lowered by approximately 1°C to 10°C.

[0212]

Such methods as described above are also described in JP-A No. 54-30032; according to these methods, moisture and an organic solvent contained in the photothermographic material can be removed out of a system and, also, deformation of the support of the photothermographic material caused by rapid heating can be

suppressed.

[0213]

### 2-3. System

As a laser imager equipped with a light exposure part and a thermal development part for the medical use, Fuji Medical Dry Imager FM-DPL is used. The system is detailed in Fuji Medical Review No. 8, pp. 39 to 55 and the techniques set forth therein are applicable. Further, the photothermographic material according to the invention may also be applied for the laser imager in "AD network", proposed by Fujifilm Medical Co., Ltd., a network system which meets the DICOM Standards.

[0214]

### 3. Application of the Invention

The photothermographic material according to the present invention forms a monochromatic silver image, and hence is preferably used in medical diagnosis, industrial photography, printing and COM (computer output microfilm).

[0215]

### [EXAMPLES]

The invention will now be illustrated by the following Examples, but it is to be understood that the invention is not limited to the Examples.

[0216]

#### Example 1

### 1. Preparation of PET Support, and Undercoat

#### 1-1. Film Formation

[0217]

From terephthalic acid and ethylene glycol, PET was produced in an ordinary manner. PET thus produced had an intrinsic viscosity, IV, of 0.66, as measured in a phenol/tetrachloroethane ratio (6/4 by weight) at 25°C. After pelletized, the PET was dried at 130°C for 4 hours, and melted at 300°C, followed by extrusion through a T-die. After rapid cooling, a non-oriented film was obtained which had a thickness of 175  $\mu\text{m}$  after thermal fixation.

[0218]

The resultant film was stretched 3.3 times in MD (machine direction) using a roll at different rotating speeds, then stretched 4.5 times in CD (cross direction) using a tenter. The temperatures for MD and CD stretchings were 110°C and 130°C, respectively. Then, the film was thermally fixed at 240°C for 20 seconds, and relaxed by 4% in CD at the same temperature. Subsequently, the chuck of the tenter was released, the both edges of the film was knurled, and the film was rolled up under 4 kg/cm<sup>2</sup> to give a rolled film having a thickness of 175  $\mu\text{m}$ .

[0219]

#### 1-2. Corona Discharge Surface Treatment

Both surfaces of the support were subjected to corona discharge treatment at room temperature at a speed of 20 m/min, using a solid-state corona discharge system MODEL 6KVA manufactured by Pillar Technologies. From the data of the current and the voltage read from the system, the support was found to be processed at 0.375 kV·A·min/m<sup>2</sup>. The frequency for the treatment was 9.6 kHz, and the gap clearance between an electrode and a dielectric roll was 1.6 mm.

[0220]

#### 1-3. Undercoat

(1) Preparation of a coating solution for an undercoat layer:

Formulation (1) (for an undercoat layer at the side of providing an image-forming layer):

- Pesuresin A-520 (a 30 % by mass solution) manufactured by Takamatsu Yushi KK

59 g

- Polyethylene glycol monononylphenyl ether (average ethylene oxide number = 8.5, a 10 % by mass solution)

5.4 g

- Polymer microparticles (MP-1000, mean particle size: 0.4 μm) manufactured by Soken Chemical & Engineering Co., Ltd.

0.91 g

- Distilled water 935 ml

[0221]

Formulation (2) (for a first back layer):

- Styrene-butadiene copolymer latex (solid content: 40 % by mass, styrene/butadiene ratio = 68/32 by mass) 158 g
- Sodium 2,4-Dichloro-6-hydroxy-S-triazine (a 8 % by mass aqueous solution) 20 g
- Sodium laurylbenzenesulfonate (a 1 % by mass aqueous solution) 10 ml
- Distilled water 854 ml

[0222]

Formulation (3) (for a second back layer):

- SnO<sub>2</sub>/SbO (9/1 by mass, mean particle size: 0.038 μm, a 17 % by mass dispersion) 84 g
- Gelatin (a 10 % aqueous solution) 89.2 g
- Metolose TC-5 (a 2 % aqueous solution) manufactured by Shin-etsu Chemical Industry Co., Ltd. 8.6 g
- MP-1000 manufactured by Soken Chemical & Engineering Co., Ltd. 0.01 g
- Sodium dodecylbenzenesulfonate (a 1 % by mass aqueous solution) 10 ml
- NaOH (1 % by mass) 6 ml
- Proxel (manufactured by ICI) 1 ml

• Distilled water

805 ml

[0223]

## (2) Coating of Undercoat

Both surfaces of the biaxially-oriented polyethylene terephthalate support (thickness: 175  $\mu\text{m}$ ) were subjected to corona discharge treatment in the same manner as above. One surface (to have an image-forming layer thereon) of the support was coated with a coating solution of the undercoat layer formulation (1) using a wire bar, and then dried at 180°C for 5 minutes to provide a wet coated amount of 6.6 ml/m<sup>2</sup> (one surface). Next, the other surface (back surface) of the support was coated with a coating solution of the back layer formulation (2) using a wire bar, and then dried at 180°C for 5 minutes to provide a wet coated amount of 5.7 ml/m<sup>2</sup>. The thus-coated back surface was further coated with the back layer formulation (3) using a wire bar, and then dried at 180°C for 6 minutes to provide a wet coated amount of 7.7 ml/m<sup>2</sup>, to finally give an undercoated support.

[0224]

## 2. Coating of Back Layer

### 2-1. Preparation of Coating solution for Back Layer

#### 1) Preparation of Solid Microparticle Dispersion (a) of Basic Precursor

64 g of a basic precursor compound-1, 10 g of “DEMOL-N” (trade name; available from Kao Corporation), 28 g of diphenylsulfone and 220 ml of distilled water were mixed. The mixture was bead



-dispersed by using 1/4G Sand Grinder Mill (available from Aimex, Ltd.) to obtain a solid fine micro particle dispersion (a) of the basic precursor compound whose mean particle diameter is 0.2  $\mu\text{m}$ .

2) Preparation of Dye Solid Microparticle Dispersion (a)

9.6 g of a cyanine dye compound-1, 5.8 g of sodium p-dodecylbenzene sulfonate, and 305 ml of distilled water were mixed. The mixture was bead-dispersed by 1/4G Sand Grinder Mill (available from Aimex, Ltd.) and to obtain a solid fine micro particle dispersion (a) whose mean particle diameter is 0.2  $\mu\text{m}$ .

[0226]

3) Preparation of Coating Solution for Antihalation Layer

17 g of gelatin, 9.6 g of polyacrylamide, 70 g of the solid microparticle dispersion (a) of the aforementioned basic precursor, and 56 g of the aforementioned dye solid microparticle dispersion (a), 1.5 g of monodisperse polymethyl methacrylate microparticles (average grain size: 8  $\mu\text{m}$ ; grain diameter standard deviation: 0.4), 0.03 g of benzoisothiazolinone, 2.2 g of sodium polyethylenesulfonate, 0.2 g of a blue dye compound-1, 3.9 g of a yellow dye compound-1 and 844 mL of water were mixed to thereby prepare a coating solution for the antihalation layer.

[0227]

#### (Preparation of Coating Solution for Protective Layer on Back Surface)

In a vessel maintained at 40°C, 50 g of gelatin, 0.2 g of sodium polystyrene sulfonate, 2.4 g of N,N-ethylene bis(vinyl sulfonamide), 1 g of sodium t-octylphenoxyethoxyethane sulfonate, 30 mg of benzoisothiazolinone, 37 mg of fluorine-type surfactant (F-1), 0.15 mg of fluorine-type surfactant (F-2), 64 mg of fluorine-type surfactant (F-3), 32 mg of fluorine-type surfactant (F-4), 8.8 g of an acrylic acid/ethylacrylate copolymer (weight ratio of copolymerization: 5/95), 0.6 g of Aerosol OT (trade name; manufactured by American Cyanamid Company), 1.8 g of a liquid paraffin emulsion in terms of liquid paraffin, and 950 ml of water were mixed to prepare a coating solution for a back surface protective layer.

[0228]

#### 2-2. Coating of Back Layer

On the back surface side of the above-described undercoated support, the thus-obtained coating solution for the anti-halation layer and the thus-obtained coating solution for the protective layer on the back surface were simultaneously applied in a superimposing manner such that quantities of gelatin applied of the coating solution for the anti-halation layer and the coating solution for the protective layer on the back surface became 0.44 g/m<sup>2</sup> and 1.7 g/m<sup>2</sup>, respectively and dried, thereby preparing the back layer.

[0229]

### 3. Image-forming layer, Intermediate Layer, and Surface Protective Layer

#### 3-1. Preparation of Material for Coating

##### 1) Preparation of Silver Halide Emulsion

[0230]

(Preparation of Comparative Silver Halide Emulsion A)

To 1,420 ml of distilled water was added 4.3 ml of a 1% by mass potassium iodide solution, followed by further addition of 3.5 ml of sulfuric acid having a concentration of 0.5 mol/L and 36.7 g of phthalated gelatin. While the resultant mixture was stirred, being maintained at 35°C, in a reaction vessel made of stainless steel, to which were added an entire amount of both a solution A which had been prepared by adding distilled water to 22.22 g of silver nitrate to be 195.6 ml and a solution B which had been prepared by adding distilled water to 21.8 g of potassium iodide to be 219 ml at a constant flow-rate for 9 minutes, followed by addition of 10 ml of a 3.5% by mass aqueous solution of hydrogen peroxide and 10.8 ml of a 10% by mass aqueous solution of benzimidazole. To the thus-prepared mixture was added a solution C which had been prepared by adding distilled water to 51.86 g of silver nitrate to be 317.5 ml and a solution D which had been prepared by adding distilled water to 60 g of potassium iodide to be 600 ml, in which an entire amount of the solution C was added at a constant flow rate for 120 minutes and the solution D was added through a controlled double jet method while

keeping a pAg value at 8.1.

[0231]

10 minutes after such additions of Solution C and Solution D were started, an entire amount of potassium hexachloroiridate (III) was added to reach  $1 \times 10^{-4}$  mol, based on 1 mol of silver. When a pH of the resultant mixture was adjusted to 3.8 using sulfuric acid having a concentration of 0.5 mol/L, a stirring operation was stopped to perform precipitation/desalting/washing steps. Then, the pH of the resultant mixture was adjusted to 5.9 using sodium hydroxide having a concentration of 1 mol/L, thereby preparing a silver halide dispersion having a pAg value of 8.0. Grains in the thus-prepared silver halide emulsion were pure silver iodide grains having an average sphere-equivalent diameter of 0.037  $\mu\text{m}$  and a variation coefficient of a sphere-equivalent diameter was 17%. Grain size was determined from an average of 1,000 grains by means of an electron microscope.

[0232]

To the silver halide dispersion was added, with stirring and maintained at 38°C, 5 ml of a 0.34% by mass methanol solution of 1,2-benzisothiazoline-3-one and, after 40 minutes elapsed, followed by further addition of  $1.2 \times 10^{-3}$  mol as a total of Spectral Sensitizing Dye A and Sensitizing Dye B, based on 1 mol of silver, of a methanol solution of a 1:1 mixture in a molar ratio of Spectral Sensitizing Dye A and Sensitizing Dye B and, after one minute elapsed, heated to 47°C.

20 minutes after the heating, to the resultant mixture was added  $7.6 \times 10^{-5}$  mol, based on 1 mol of silver, of a methanol solution of sodium benzene thiosulfonate. Further, after 5 minutes elapsed, a pAg of the resultant mixture was adjusted to be 5.5, and then to the mixture was added  $5.1 \times 10^{-4}$  mol, based on 1 mol of silver, of a tellurium sensitizing agent (bis(N-phenyl-N-methyl carbamoyl) telluride) and, thereafter, ripened for 84 minutes. After the pAg of the resultant mixture was adjusted to be 7.5, the mixture was added 1.3 ml of a 0.8% by mass methanol solution of N,N'-dihydroxy-N''-diethylmelamine and, further, after 4 minutes elapsed, added with  $4.8 \times 10^{-3}$  mol, based on 1 mol of silver, of a methanol solution of 5-methyl-2-mercaptobenzimidazole and  $5.4 \times 10^{-3}$  mol, based on 1 mol of silver, of a methanol solution of 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole to prepare Comparative Silver Halide Emulsion A.

[0233]

(Preparation of Comparative Silver Halide Emulsion B)

Comparative Silver Halide Emulsion B was prepared in the same manner as Comparative Silver Halide Emulsion A, except that an entire amount of an aqueous solution of potassium hexacyanoiron (II) was added instead of potassium hexachloroiridate (III) to reach  $3 \times 10^{-3}$  mol, based on 1 mol of silver.

[0234]

(Preparation of Comparative Silver Halide Emulsion C)

Comparative Silver Halide Emulsion C was prepared in the same manner as Comparative Silver Halide Emulsion A, except that potassium hexachloroiridate (III) was removed therefrom.

[0235]

(Preparation of Silver Halide Emulsions-1 to 7 according to the Present Invention)

<Emulsion-1: Ir/Fe (Ir: uniform; Fe: uniform)>

Silver Halide Emulsion-1 according to the invention was prepared in the same manner as Comparative Silver Halide Emulsion A, except that potassium hexachloroiridate (III) and an aqueous solution of potassium hexacyanoiron (II) were added to Solution C and Solution D, respectively, to render them uniformly doped in quantities of  $5 \times 10^{-4}$  mol and  $5 \times 10^{-3}$  mol, based on 1 mol of silver, respectively.

<Emulsion-2: Ir/Fe (Ir: core; Fe: shell)>

Silver Halide Emulsion-2 according to the invention was prepared in the same manner as Silver Halide Emulsion 1 according to the invention, except that an aqueous solution of potassium hexachloroiridate (III) was added only to Solution C instead of Solutions C and D to render it doped in a core portion and, also, an aqueous solution of potassium hexacyanoiron (II) only to Solution D instead of Solution C and D to render it doped in a shell portion.

<Emulsion-3: Ir/Fe (Ir: core; Fe: surface)>

Silver Halide Emulsion-3 according to the invention was

prepared in the same manner as Silver Halide Emulsion-1 according to the invention, except that an aqueous solution of potassium hexacyanoiron (II) was added directly to a grain-forming reaction vessel after a grain has been formed instead of Solutions C and D.

<Emulsion-4: Ru/Fe (Ru: core; Fe: surface)>

Silver Halide Emulsion-4 according to the invention was prepared in the same manner as Silver Halide Emulsion-3' according to the invention except that an aqueous solution of potassium hexachlororuthenate (II) was added instead of a solution of potassium hexachloroiridate (III) to reach  $5 \times 10^{-4}$  mol, based on 1 mol of silver.

<Emulsion-5: Cu/Fe (Cu: core; Fe: surface)>

Silver Halide Emulsion-5' according to the invention was prepared in the same manner as Silver Halide Emulsion-3' according to the invention, except that an aqueous solution of copper (III) nitrate was added instead of a solution of potassium hexachloroiridate (III) to reach  $5 \times 10^{-4}$  mol, based on 1 mol of silver.

<Emulsion-6: Fe/Pt (Fe: core; Pt: surface)>

Silver Halide Emulsion-6 according to the invention was prepared in the same manner as Silver Halide Emulsion-5 according to the invention, except that an aqueous solution of hexacyanoiron (II) was added instead of an aqueous solution of copper (II) nitrate to reach  $5 \times 10^{-3}$  mol, based on 1 mol of silver and, also, an aqueous solution of potassium tetrachloroplatinate (II) was added instead of an aqueous solution of potassium hexacyanoiron (II) to reach  $5 \times 10^{-3}$  mol, based on 1 mol of silver.

<Emulsion-7: Os/Fe (Os: core; Fe: surface)>

Silver Halide Emulsion-7 according to the invention was prepared in the same manner as Silver Halide Emulsion-4 according to the invention, except that an aqueous solution of potassium hexachloroosmate (III) was added instead of an aqueous solution of potassium hexaiodoruthenate (II) to reach  $5 \times 10^{-4}$  mol, based on 1 mol of silver.

[0236]

(Preparation of Emulsions 1a to 1c, and 1 to 7 for Addition to Coating Solution)

Silver halide emulsions thus obtained were separated into a plurality of small portions and dissolved and, then, 1-(3-methylureido) phenyl-5-mercaptotetrazole was added to each of the thus-separated silver halide emulsions to reach  $5 \times 10^{-3}$  mol therein, based on 1 mol of silver, to which was added water to make a silver halide content, based on 1 kg of an emulsion for addition to a coating solution, to be 38.2 g in terms of silver.

[0237]

2) Preparation of Fatty Acid Silver Dispersion

87.6 kg of behenic acid (product name: Edenor C22-85R; manufactured by Henkel Co.), 423 L of distilled water, 49.2 L of an aqueous solution of NaOH having a concentration of 5 mol/L and 120 L of t-butyl alcohol were mixed and, then, allowed to react with one



another, while being stirred at 75°C for 1 hour, to obtain a sodium behenate solution. Apart from the sodium behenate solution, 206.2 L of an aqueous solution (pH: 4.0) containing 40.4 kg of silver nitrate was prepared and maintained at 10°C. A reaction vessel charged with 635 L of distilled water and 30 L of t-butyl alcohol was maintained at 30°C and, then, while being sufficiently stirred, charged with an entire amount of the foregoing sodium behenate solution and an entire amount of the foregoing silver nitrate aqueous solution at a constant flow rate for 93 minutes 15 seconds and 90 minutes, respectively. At that time, the silver nitrate aqueous solution was solely added for 11 minutes after the addition of the silver nitrate aqueous solution was started. After that, the addition of the sodium behenate solution was started. For 14 minutes 15 seconds after the addition of the silver nitrate aqueous solution was completed, the sodium behenate solution was solely added. At that time, a temperature inside the reaction vessel was maintained at 30°C and a solution temperature was maintained constant by means of an external temperature control. Further, piping of an addition system for the sodium behenate solution was warmed by circulating warm water in an outer part of a double-walled tube so that the solution temperature at an outlet of an addition nozzle tip was adjusted to be 75°C. Piping of an addition system of the aqueous silver nitrate solution was also heat-controlled by circulating cold water in an outer part of a double-walled tube. Positions where the sodium behenate solution and the aqueous silver nitrate solution were added were arranged symmetrically in relation to

a stirring shaft in the center, and respective heights of the positions were adjusted such that they do not touch a reaction solution.

[0238]

After the addition of the sodium behenate solution was completed, the resultant reaction solution was held at a temperature thereof as it was for 20 minutes with stirring and, then, the temperature was elevated up to 35°C for 30 minutes. After that, the reaction solution was ripened for 210 minutes. Immediately after such ripening, the solids were separated by centrifugal filtration and, then, the thus-separated solids were rinsed with water until electrical conductivity of the filtrate reached 30  $\mu\text{S}/\text{cm}$ . Thus, a fatty acid silver salt was obtained. The solids obtained in such a manner as described above was stored as a wet cake without drying.

[0239]

Shapes of silver behenate particles thus obtained were evaluated by electron microscopic photography. The obtained silver behenate particles were flaky crystals having average values of  $a=0.14\ \mu\text{m}$ ,  $b=0.4\ \mu\text{m}$  and  $c=0.6\ \mu\text{m}$ , an average aspect ratio of 5.2, an average sphere-equivalent diameter of  $0.52\ \mu\text{m}$ , and a variation coefficient of a sphere-equivalent diameter of 15% ( $a$ ,  $b$  and  $c$  were defined according to respective definitions previously described herein).

[0240]

19.3 kg of polyvinyl alcohol (trade name: PVA-217; manufactured by Kuraray Co., Ltd.) and water were added to the wet cake corresponding to 260 kg of dried solid content to make an entire amount of the resultant mixture up to be 1,000 kg and, then, the resultant mixture was formed into a slurry using dissolver-blades. Further, the slurry was preliminarily dispersed with a pipeline-mixer (Model PM-10; manufactured by Mizuho Industrial Co., Ltd.)

[0241]

Then, a stock solution thus preliminarily dispersed was processed three times with a dispersing machine (trade name: Microfluidizer M-610 equipped with a Z-type interaction chamber; manufactured by Microfluidex International Corporation) under a pressure adjusted to 1,260 kg/cm<sup>2</sup> to obtain a silver behenate dispersion. A dispersion temperature was set at 18°C by adjusting a temperature of coolant such that a cooling operation was performed using coil type heat exchangers installed in front and rear of the interaction chamber, respectively.

[0242]

### 3) Preparation of Reducing Agent Dispersion (a)

7.2 kg of water was added to 10 kg of Reducing Agent Complex-1, 0.12 kg of triphenyl phosphine oxide, and 16 kg of a 10% by mass aqueous solution of modified polyvinylalcohol (trade name: POVAL MP203; manufactured by Kuraray Co. Ltd.). Then, the

resultant mixture was thoroughly mixed into a slurry. The slurry was fed by means of a diaphragm pump into a horizontal-type sand mill (trade name: UVM-2; manufactured by Imex Co., Ltd.) filled with zirconia beads having an average diameter of 0.5 mm, and dispersed for 4 hours 30 minutes. Then, 0.2 g of a sodium salt of benzoisothiazolinone and water were added to the resultant dispersion so as to make a concentration of the reducing agent complex to be 25% by mass, thereby obtaining a Reducing Agent Complex-1 Dispersion (a). Particles of the reducing agent complex contained in the reducing agent complex dispersion thus obtained had a median particle diameter of 0.46  $\mu\text{m}$  and a maximum particle diameter of 1.6  $\mu\text{m}$  or less. The thus-obtained reducing agent complex dispersion was filtrated with a filter made of polypropylene having a pore diameter of 3.0  $\mu\text{m}$  to remove foreign matters such as dust and, then, stored.

[0243]

#### 4) Preparation of Polyhalogen Compound

(Preparation of Organic Polyhalogen Compound Dispersion (a))

14 kg of water was added to 10 kg of Organic Polyhalogen Compound-1, 10 kg of a 20% by mass aqueous solution of modified polyvinylalcohol (trade name: POVAL MP203; manufactured by Kuraray Co., Ltd.), and 0.4 kg of a 20% by mass aqueous solution of sodium triisopropylphenyl sulfonate. Then, the resultant mixture was thoroughly mixed to form a slurry. The slurry was fed by means of a diaphragm pump into a horizontal-type sand mill (trade

name: UVM-2; manufactured by Imex Co., Ltd.) filled with zirconia beads having an average diameter of 0.5 mm, and dispersed for 5 hours. Then, 0.2 g of a sodium salt of benzoisothiazolinone and water were added to such a dispersion so as to make a concentration of the organic polyhalogen compound to be 26% by mass, thereby obtaining Organic Polyhalogen Compound Dispersion (a). Particles of the organic polyhalogen compound contained in the organic polyhalogen compound dispersion thus obtained had a median particle diameter of 0.41  $\mu\text{m}$  and a maximum particle diameter of 2.0  $\mu\text{m}$  or less. The organic polyhalogen Compound dispersion obtained above was filtrated with a filter made of polypropylene having a pore diameter of 10.0  $\mu\text{m}$  to remove foreign matters such as dust and, then, stored.

[0244]

(Preparation of Organic Polyhalogen Compound Dispersion (b))

10 kg of Organic Polyhalogen Compound-2, 20 kg of a 10% by mass aqueous solution of modified polyvinylalcohol (trade name: POVAL MP203; manufactured by Kuraray Co., Ltd.), 0.4 kg of a 20% by mass aqueous solution of sodium triisopropylnaphthalene sulfonate, and 8 kg of water were thoroughly mixed to form a slurry. The slurry was fed by means of a diaphragm pump into a horizontal-type sand mill (trade name: UVM-2; manufactured by Imex Co., Ltd.) filled with zirconia beads having an average diameter of 0.5 mm, and dispersed for 5 hours. Then, 0.2 g of a sodium salt of benzoisothiazolinone and water were added to such a dispersion so as to make a concentration

of the organic polyhalogen compound to be 25% by mass. The resultant dispersion was heated at 40°C for 5 hours to obtain Organic Polyhalogen Compound-3 Dispersion. Particles of the organic polyhalogen compound contained in the organic polyhalogen compound dispersion thus obtained had a median particle diameter of 0.36  $\mu\text{m}$  and a maximum particle diameter of 1.5  $\mu\text{m}$  or less. The organic polyhalogen compound dispersion thus obtained was filtrated with a filter made of polypropylene having a pore diameter of 3.0  $\mu\text{m}$  to remove foreign matters such as dust and, then, stored.

[0245]

#### 6) Preparation of Phthalazine Compound-1 Solution

8 kg of modified polyvinylalcohol (trade name: MP203; manufactured by Kuraray Co., Ltd.) was dissolved in 174.57 kg of water. Then, 3.15 kg of a 20% by mass aqueous solution of sodium triisopropylphthalene sulfonate and 14.28 kg of a 70% by mass aqueous solution of Phthalazine Compound-1 (6-isopropylphthalazine) were added to the resultant solution to prepare a 5% by mass solution of Phthalazine Compound-1.

[0246]

#### 7) Preparation of Aqueous Solution of Mercapto Compound-1

7 g of Mercapto Compound-1 was dissolved in 993 g of water to prepare a 0.7% by mass aqueous solution.

[0247]

#### 8) Preparation of Pigment-1 Dispersion

250 g of water was added to 64 g of C.I. Pigment Blue 60 and 6.4 g of DEMOL N (trade name; manufactured by Kao Corporation). Then, the resultant mixture was thoroughly mixed to form a slurry. 800 g of zirconia beads having an average diameter of 0.5 mm was prepared and charged in a vessel together with the slurry. The slurry was dispersed for 25 hours using a dispersing machine (trade name: 1/4 G Sand-Grinder Mill; manufactured by Imex Co., Ltd.) and, then, taken out of the vessel, to which was added water to make a concentration of such pigment to be a 5% by mass, thereby obtaining Pigment-1 Dispersion. Pigment particles contained in the pigment dispersion thus obtained had an average particle diameter of 0.21  $\mu\text{m}$ .

[0248]

#### 9) Preparation of SBR Latex Solution

An SBR latex at  $T_g=23^\circ\text{C}$  was prepared in the following manner. 70.5 parts by mass of styrene, 26.5 parts by mass of butadiene, and 3 parts by mass of acrylic acid were subjected to emulsion polymerization using ammonium persulfate as a polymerization initiator and an anionic surfactant as an emulsifying agent and, then, the resultant reaction product was aged at  $80^\circ\text{C}$  for 8 hours. Thereafter, the reaction product was cooled to  $40^\circ\text{C}$  and, then, a pH thereof was brought to 7.0. Further, to the resultant mixture was added SANDET BL (trade name; manufactured by Sanyo Chemical

Industries, Ltd.) to give a concentration of 0.22%. A pH of the resultant mixture was adjusted to 8.3 using an aqueous 5% NaOH solution, further, adjusted to 8.4 using an aqueous ammonia solution, in which a molar ratio of Na<sup>+</sup> ion to NH<sub>4</sub><sup>+</sup> ion was employed was 1:2.3.

Still further, 0.15 ml of an aqueous 7% solution of a sodium salt of benzoisothiazolinone was added to the thus-pH-adjusted mixture, thereby preparing an SBR latex solution.

[0249]

(SBR latex: latex of -St(70.5)-Bu(26.5)-AA(3))

The latex was found to be as follows: an average particle diameter at T<sub>g</sub>=23°C: 0.1 μm; concentration: 43% by mass; equilibrium moisture content at 25°C 60% RH: 0.6% by mass; ionic conductance: 4.2 mS/cm (as for ionic conductance, latex starting solution (43% by mass) was measured at 25°C using a diaphragm (trade name: CM-30S; manufactured by Toa Denpa Kogyo Co., Ltd.)); and pH: 8.4.

SBR latices having different T<sub>g</sub> have been prepared in the same manner as described above, with properly changing ratios between styrene and butadiene.

[0250]

### 3-2. Preparation of Coating Solution

#### 1) Preparation of Coating Solution for Image-forming layer

1,000 g of Fatty Acid Silver Salt Dispersion obtained in a manner as described above, 104 ml of water, 30 g of Pigment-1



Dispersion, 6.3 g of Organic Polyhalogen Compound (a) Dispersion, 20.7 g of Organic Polyhalogen Compound (b) Dispersion, 173 g of Phthalazine Compound-1 Solution, 1,082 g of SBR Latex (Tg: 23°C) Solution, 258 g of Reducing Agent Dispersion (a), and 9 g of Mercapto Compound Solution were added in this order. Immediately before coating, each of emulsions for addition to coating solutions was added to the resultant mixture such that an amount thereof became 6.6% in a molar ratio in terms of silver against the organic acid silver to prepare each of well-mixed coating solutions 1a to 1c, and 1 to 7 for image-forming layers. Each of the thus-obtained coating solutions for image-forming layers was fed into a coating die as it was to be applied.

[0251]

## 2) Preparation of Coating Solution for Intermediate Layer

2 ml of a 5% by mass aqueous solution of Aerosol OT (trade name; manufactured by American Cyanamid Company) and 10.5 ml of a 20% by mass aqueous solution of diammonium phthalate were added to 772 g of a 10% by mass aqueous solution of polyvinyl alcohol (trade name: PVA-205; manufactured by Kuraray Co., Ltd.), 5.3 g of Pigment-1 Dispersion, and 226 g of a 27.5% by mass solution of a latex of a methyl methacrylate/styrene/butyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization ratio by weight: 64/9/20/5/2) and, then, water was added to the resultant mixture to make an entire amount thereof up to be 880 g. A pH value of the thus-made mixture was adjusted to 7.5 using NaOH, thereby obtaining

a coating solution for an intermediate layer. The coating solution was fed into a coating die such that a coating amount became 10 ml/m<sup>2</sup>.

Viscosity of the coating solution measured by a B-type viscometer (No. 1 rotor at 60 rpm) was 65 [mPa·s] at 40°C.

[0252]

### 3) Preparation of Coating Solution for First Layer of Surface Protective Layer

64 g of inert gelatin was dissolved in water. To the resultant gelatin solution were added 80 g of a 27.5% by mass solution of a latex of a methyl methacrylate/styrene/butyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization ratio by weight: 64/9/20/5/2), 23 ml of a 10% by mass methanol solution of phthalic acid, 23 ml of a 10% by mass aqueous solution of 4-methyl phthalic acid, 28 ml of sulfuric acid having a concentration of 0.5 mol/L, 5 ml of a 5% by mass aqueous solution of Aerosol OT (trade name; manufactured by American Cyanamid Company), 0.5 g of phenoxyethanol and 0.1 g of benzoisothiazolinone. Then, water was added to the resultant mixture to make an entire amount thereof up to be 750 g, thereby obtaining a coating solution. Immediately before coating, the coating solution was mixed with 26 ml of a 4% by mass chrome alum solution using a static mixer and, then, fed to a coating die such that a coating amount became 18.6 ml/m<sup>2</sup>.

Viscosity of the coating solution measured by a B-type viscometer (No. 1 rotor at 60 rpm) was 20 [mPa·s] at 40°C.

[0253]

#### 4) Preparation of Coating Solution for Second Layer of Surface Protective Layer

80 g of inert gelatin was dissolved in water. To the resultant gelatin solution were added 102 g of a 27.5% by mass solution of a latex of a methyl methacrylate/styrene/butyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization ratio by weight: 64/9/20/5/2), 3.2 ml of a 5% by mass solution of a fluorine-type surfactant (F-1), 32 ml of a 2% by mass aqueous solution of a fluorine-type surfactant (F-2), 23 ml of a 5% by mass solution of Aerosol OT (trade name; manufactured by American Cyanamid Company), 4 g of polymethyl methacrylate fine particles (average particle diameter: 0.7  $\mu\text{m}$ ), 21 g of polymethyl methacrylate fine particles (average particle diameter: 4.5  $\mu\text{m}$ ), 1.6 g of 4-methyl phthalic acid, 4.8 g of phthalic acid, 44 ml of sulfuric acid having a concentration of 0.5 mol/L, and 10 mg of benzoisothiazolinone. Then, water was added to the resultant mixture to make an entire amount thereof up to be 650 g, thereby obtaining a mixture. Immediately before coating, to the thus-obtained mixture was further added 445 ml of an aqueous solution containing 4% by mass of chrome alum and 0.67% by mass of phthalic acid using a static mixer to obtain a coating solution for a second surface protective layer. The thus-obtained coating solution for the second surface protective layer was fed into a coating die such that a coating amount became 8.3 ml/m<sup>2</sup>.

Viscosity of the coating solution measured by a B-type viscometer (No. 1 rotor at 60 rpm) was 19 [mPa·s] at 40°C.

[0254]

### 3-3. Preparation of Photothermographic Materials 1a to 1c, and 1 to 7

[0255]

On a surface opposite to a back surface, coating solutions each for an image-forming layer, an intermediate layer, a first surface protective layer, and a second surface protective layer were simultaneously applied through a slide bead coating method in this order to prepare the samples of photothermographic materials. Temperatures, at that time, of coating solutions were adjusted such that the coating solution for the image-forming layer and that for the intermediate layer were maintained at 35°C, that for the first surface protective layer was maintained at 36°C, and that for the second surface protective layer was maintained at 37°C.

Coating amount (g/m<sup>2</sup>) of each compound in the image-forming layer is shown below.

[0256]

Silver behenate	6.19
Pigment (C.I.Pigment Blue 60)	0.036
Polyhalogen Compound-1	0.04
Polyhalogen Compound-2	0.12

Phthalazine Compound-1	0.21
SBR latex	11.1
Reducing Agent Complex-1	1.54
Mercapto Compound-1	0.002
Silver halide (in terms of silver)	0.10
Each of compounds of types 1 to 4 (shown in table 1)	
	$1 \times 10^{-3}$ mol per mol of
silver halide	

[0257]

Coating and drying conditions are described below.

Coating was performed at a coating speed of 160 m/min. A distance between the tip of the coating die and the support was set in the range of from 0.10 mm to 0.30 mm. Pressure inside a reduced pressure chamber was set lower than the atmospheric pressure by from 196 Pa to 882 Pa. The support was destaticized with ionized air before coating.

After the coated solution was cooled in a subsequent chilling zone with air having a dry bulb temperature of from 10°C to 20°C, the coated support was transported to a helical non-contact-type drying apparatus in a non-contact manner and, then, dried therein with drying air having a dry bulb temperature of from 23°C to 45°C and a wet bulb temperature of from 15°C to 21°C to obtain coated samples 21 to 27.

After such drying, the thus-obtained samples were conditioned

in moisture contents at 25°C from 40% to 60% RH and, then, heated such that a temperature of each of surfaces thereof was elevated to 70°C -90°C and, subsequently, cooled such that the temperature of the surface was lowered to 25°C.

[0258]

Matte degrees of the thus-prepared photothermographic material were 550 seconds on the side of the surface of the image-forming layer and 130 seconds on the side of the back surface in terms of Beck's smoothness. The pH value of such a film surface on the side of the image-forming layer was measured and found to be 6.0.

[0259]

Chemical structures of compounds used in Examples are shown below.

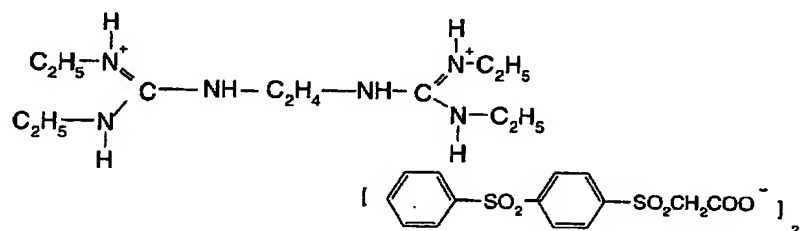
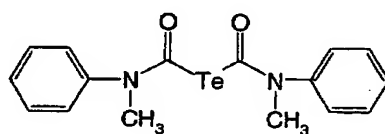
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[F11]

22



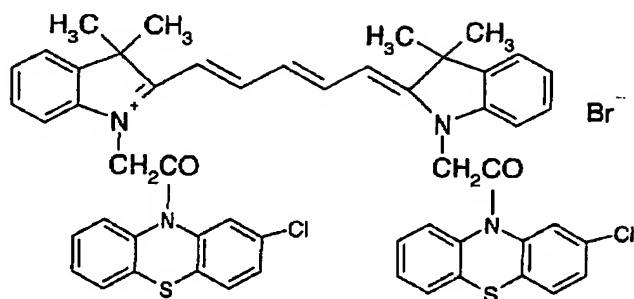
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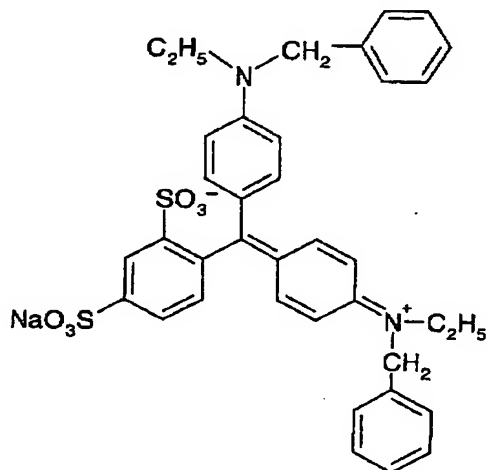
10

50

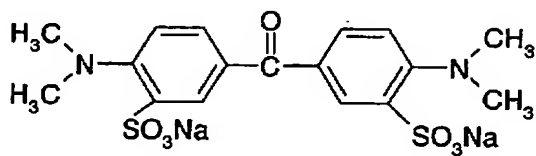
CYANINE DYE COMPOUND-1



BLUE DYE COMPOUND-1



YELLOW DYE COMPOUND-1

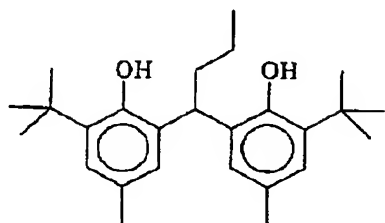


[0262]

[F13]

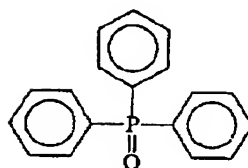


(Reducing Agent Complex-1)

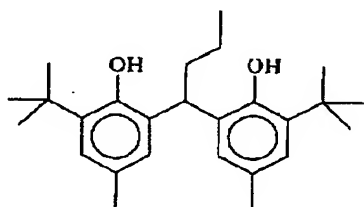


and

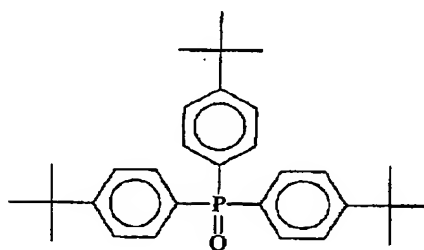
1:1 complex of



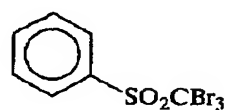
(Reducing agent-2)



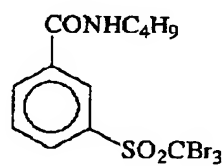
(Hydrogen bond-forming Compound-1)



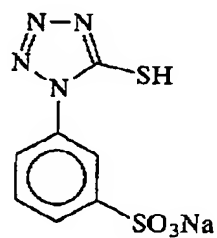
(Polyhalogen Compound-1)



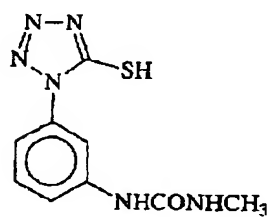
(Polyhalogen Compound-2)



(Mercapto Compound-1)



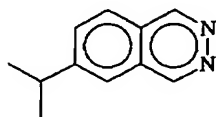
(Mercapto Compound-2)



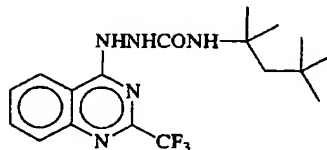
[0263]

[F14]

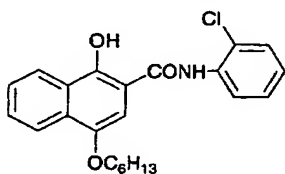
(Phthalazine Compound-1)



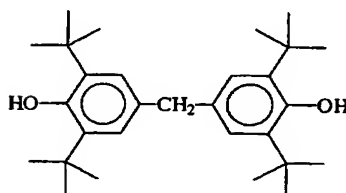
(Developing Accelerator-1)



(Developing Accelerator-2)

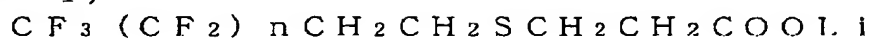


(Color Tone Controlling Agent-1)



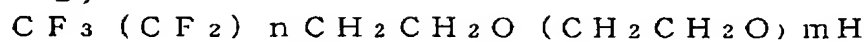
[0264] [F15]

( F - 1 )



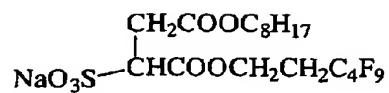
Mixture of n=5 to 11

( F - 2 )

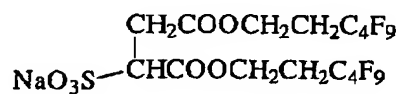


Mixture of n=5 to 11, m=5 to 15

( F - 3 )



( F - 4 )



[0265]

#### 4. Evaluation of Photographic Performance

##### (Preparation)

Each of the thus-obtained samples was cut into 20 x 12 inch sized sheets, packed with a packaging material mentioned below at 25°C 50% RH and, then, stored for 2 weeks at room temperature.

##### (Packaging Material)

The packaging material used was 50  $\mu\text{m}$  thick polyethylene film comprising 10  $\mu\text{m}$  PET/12  $\mu\text{m}$  PE/9  $\mu\text{m}$  aluminum foil/15  $\mu\text{m}$  Ny/50  $\mu\text{m}$  polyethylene containing 3% carbon.

Oxygen transmittance was 0.02 ml/atm·m<sup>2</sup>·25°C·day; and moisture transmittance was 0.10 g/atm·m<sup>2</sup>·25°C·day.

[0266]

The above described photothermographic material was assessed according to the tests mentioned below.

##### (Exposure of Photothermographic Material)

The photothermographic material was exposed to light in the following manner.

Using a modified Fuji Medical Dry Laser Image FM-DP L, the obtained photothermographic materials were exposed to light and subjected to development treatment.

The exposure was conducted by irradiating such photosensitive material with a 660 nm semiconductor laser having a maximum output of 60 mW (IIIB) in a manner of focusing in an area of 100  $\mu\text{m}$  x

100  $\mu\text{m}$ . The exposure was conducted with stepwise changing irradiation quantities of laser. The development was conducted by means of a thermal development part of the FM-DP L, with using four plates of panel heaters therein which had respectively been set at 112°C, 119°C, 121°C, and 121°C in which an entire developing time was 24 seconds.

[0267]

(Evaluation of Samples)

Density of the resultant image was measured using a Macbeth densitometer to prepare a characteristic curve of the density to a logarithm of exposed amount.

Sensitivity:

Sensitivity was denoted in terms of a reciprocal number of exposed amount necessary to provide a blackening density of fog+1.0 and is shown as a relative value taking the sensitivity of Sample No. 1 to be 100. Incidentally, as the value becomes larger, the sensitivity becomes higher.

Dmin:

Density of a non-image portion was measured using a Macbeth densitometer.

Storage Properties of Image:

The samples which have been thermally developed were cut into 20×12 inch sized sheets and kept under an illumination intensity of 1000 lux using a fluorescent light for 24 hours in an atmosphere of

30°C 70% RH. An increase in density at a Dmin portion as compared with that before such a treatment was evaluated.

[0268]

The results are shown in Table 1.

As is apparent from the results, it is revealed that the photothermographic material according to the invention exhibits high sensitivity and a low level of Dmin by doping two or more metals therein and further maintains a good level of printout performance after thermal development, which is obtained when using a silver iodide emulsion.

[0269]

[Table 1]

Sample No.	Dmin	Sensitivity	Printout performance( $\Delta$ Dmin)	Remarks
1a	0.17	95	0.12	Comparative Example
1b	0.17	98	0.11	Comparative Example
1c	0.19	100	0.14	Comparative Example
1	0.17	105	0.09	Present Invention
2	0.16	106	0.08	Present Invention
3	0.16	108	0.07	Present Invention
4	0.17	107	0.07	Present Invention
5	0.16	108	0.06	Present Invention
6	0.16	108	0.07	Present Invention
7	0.17	107	0.07	Present Invention

[0270]

Example 2

Coated samples 2a, 2b, 21 to 27 were obtained in the same manner as the silver halide emulsion in Example 1, except that a silver

iodide emulsion was prepared without adding Sensitizing Dyes A and B. Thereafter, the samples were subjected to the same treatments as in Example 1 except for using 405 nm blue laser light to thereby obtain the results shown in Table 2. Incidentally, sensitivity is shown as a relative value taking the sensitivity of sample No. 21 to be 100.

[0271]

[Table 2]

Sample No.	Dmin	Sensitivity	Printout performance ( $\Delta D_{\min}$ )	Remarks
2a	0.15	102	0.11	Comparative Example
2b	0.15	103	0.10	Comparative Example
2c	0.16	100	0.13	Comparative Example
21	0.14	107	0.08	Present Invention
22	0.14	108	0.07	Present Invention
23	0.13	108	0.07	Present Invention
24	0.14	108	0.07	Present Invention
25	0.14	109	0.06	Present Invention
26	0.14	108	0.07	Present Invention
27	0.14	109	0.07	Present Invention

[0272]

As is apparent from the results shown in Table 2, it is revealed that the photothermographic material according to the invention exhibits high sensitivity and a low level of Dmin by doping two or more metals therein, and further maintains a good level of printout performance after thermal development, which is obtained when using a silver iodide emulsion.

[0273]

Example 3

An emulsion was prepared in the same manner as in Example 1, except that types of doped metals in a photosensitive silver halide emulsion were changed to those as shown in Table 3. A first metal and a second metal were added, based on 1 mol of silver, in quantities of  $5 \times 10^{-4}$  mol and  $3 \times 10^{-3}$  mol, respectively.

[0274]

The results obtained and evaluated in the same manner as in Example 1 are shown in Table 3. Sensitivity is shown as a relative value, taking the first metal used alone to be 100, such that the effect exerted by simultaneous doping of two species of metals may be represented. In the same manner as in Example 1, it is revealed that the photothermographic material according to the invention exhibits high sensitivity and a low level of Dmin by doping two metals therein and further maintains a good level of printout performance after thermal development, which is obtained when using a silver iodide emulsion.

[0275]

[Table 3]

Sample No.	First Metal	Second Metal	Dmin	Sensitivity	Printout Performance	Remarks
3a	Ir	-	0.17	100	0.11	Comparative Example
3b	-	Fe	0.17	103	0.10	Comparative Example
3	Ir	Fe	0.16	107	0.07	Present Invention
5a	Cu	-	0.17	101	0.10	Comparative Example
5b	-	Fe	0.17	102	0.10	Comparative Example
5	Cu	Fe	0.16	105	0.07	Present Invention
6a	Fe	-	0.17	101	0.10	Comparative Example
6b	-	Pt	0.17	102	0.10	Comparative Example
6	Fe	Pt	0.16	106	0.08	Present Invention
7a	Os	-	0.17	100	0.10	Comparative Example
7b	-	Fe	0.17	103	0.10	Comparative Example
7	Os	Fe	0.16	106	0.07	Present Invention

[0276]

[Effects of the Invention]

As detailed above, the present invention provides a photothermographic material which is excellent in printout performance and lightfastness of images after processing and exhibits high sensitivity and low Dmin.



[DOCUMENT NAME] ABSTRACT OF THE DISCLOSURE

[SUMMARY]

[OBJECT]

To provide a photothermographic material that exhibits high sensitivity and which is excellent in lightfastness of images after receiving development treatment.

[MEANS FOR SOLUTION]

A photothermographic material comprising a support including on one surface thereof at least a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent for reducing silver ions and a binder, wherein the photosensitive silver halide 1) has a silver iodide content ranging from 40 mol% to 100 mol%, and 2) contains two species or more comprising at least one metal selected from the following first metal group and at least one metal selected from the following second metal group:

(First metal group)

iridium, ruthenium, iron, osmium and copper;

(Second metal group)

iridium, ruthenium, iron, osmium, rhenium, gold, platinum, copper, indium, gallium, lead, thallium, chromium, palladium, nickel and zinc,

wherein none of the at least one metal selected from the first metal group and the at least one metal selected from the second metal group are the same.

[SELECTED FIGURE] None